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Introduction to
TEXTILE CHEMISTRY

BOOKS BY BRUCE E. HARTSUCH

INTRODUCTION TO TEXTILE CHEMISTRY

TEXTILE CHEMISTRY IN THE LABORATORY

ELEMENTARY QUALITATIVE ANALYSIS

Introduction to
TEXTILE CHEMISTRY

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PREFACE

During recent years there has been an increasing awareness that something revolutionary has occurred in the field of textiles. New fibers and filaments have made their appearance; the wizardry of the textile chemist and engineer has produced fibers from such raw materials as soybeans, corn, skim milk, chicken feathers and benzene; old fibers have been improved; wool has been torn down and rebuilt so that many of its undesirable properties have been lost; rayons of exceptionally high strength are being manufactured; new finishes for textiles have been produced in an array that revolutionizes the types and properties of our textile materials, so that we now have shrink-resistant wool, mothproof wool, fire-resistant cotton, and cotton cloths that will not shrink; and our knowledge of the fine structure of cellulosic and protein fibers has increased to such an extent that we have begun to feel really acquainted with these complex materials.

It is no wonder that colleges have a definite conviction that students of textiles should have a broad training in the fundamentals of the raw materials with which they will work. The information on all these topics is voluminous and is scattered through many journals in three or four languages. The need for a book on textile chemistry is apparent to anyone connected with the manufacture and maintenance of textile materials, especially those who are students and teachers in the educational branch of this field.

I have made an effort to bring between the covers of one book the most basic and pertinent information on textile fibers and their relation to everyday living, including their history and development, their physical and chemical properties, processing, and manufacturing, and their expected behavior under the various conditions to which they may be exposed.

This book has been designed and written as a textbook for college students and teachers who have a knowledge of the theoretical and applied chemistry that forms the foundation for the development of every student entering the field of textiles, whether it be in teaching, technology, fabric manufacture, fabric maintenance, consumer service, or general research.

Although textile chemistry should be taught in colleges where courses in clothing and textiles are offered, it should not be intended to train students as experts but rather to give them background and foundation and the ability to read the literature of their field intelligently.

In order to accomplish these purposes this book has been written (*a*) as a textbook for a specific college course and (*b*) as a somewhat detailed and extended discussion, part of which may not be required in a formal course but may be valuable to a student at some later time.

Although the book has been written with the college student constantly in mind, it is hoped that the technologist may find some use for it and that even the specialist may derive some benefit from it in fields outside his own. Since the emphasis is definitely on the chemistry of the raw materials used in the textile field, some persons may find it useful for adding to their knowledge of chemistry as applied to textiles. Such persons may also find the glossary helpful.

I have selected topics that I think will be most valuable and will sharpen students' interest and broaden their knowledge of the raw materials with which their major problems are concerned. Adequate discussions of cotton, wool, silk, and rayon are included, as well as a chapter on the chemistry of cellulose as related to textiles. The six important synthetic fibers are covered in three chapters. One chapter is devoted to a discussion of the physical aspects of textile materials and the essential properties of fibers, such as staple, strength, elongation, and elastic recovery.

The book has some advantageous special features. It is well known that many students have trouble with problems, especially problems dealing with chemical calculations. For this reason a chapter on simple chemical calculations has been included. This chapter deals with the mechanics of percentages, proportions, etc., and their application to problems in textile chemistry. The principles are explained, examples are given, and about seventy-five problems, which may be assigned to students, are listed. A chapter on organic chemistry insures a good understanding of the many organic reactions met in textile chemistry. This chapter has been written so that a student who has never had any organic chemistry will get enough information to carry through with this subject.

The importance of soap and water in the manufacture, and especially in the maintenance, of textiles has never been sufficiently emphasized. Therefore, two chapters on these pertinent subjects discuss their chemistry and applications in the textile field.

As each science has its own vocabulary, some of the terms used in textile chemistry will be new to the reader. It is obvious that intelligent and accurate reading cannot be done without a knowledge of the vocabulary being used, and therefore I have appended an adequate glossary.

One will find many statements repeated in this book. This is done (*a*) because one learns by repetition and (*b*) so that the reading may be done from the index, or so that some particular chapter may be read without studying previous chapters. Another characteristic to be noted is that the first few chapters are quite pedagogical, but this style is changed in the later chapters. It is felt that the formalized style is proper for the beginning of such study, but, since we learn as we go, the later chapters need not be so methodical.

It is, of course, impossible to concentrate the entire field of textile chemistry into one book, and, therefore, many things have been omitted. Among these is the subject of dyes and dyeing. I am of the opinion that the manufacture and application of dyes are highly specialized fields, involving advanced chemistry, and are therefore unsuitable for the students who will normally use this book.

I am sincerely interested in the development of a book of this type because there is a great need and latent demand for it. Consequently, all pro and con comments will be greatly appreciated.

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June 1950

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1 · Calculations Used in Chemistry

This chapter may be considered as a refresher course in a few simple types of arithmetical calculations and some typical calculations used in chemistry. Many students will have forgotten how to handle some of these problems, and so we strongly urge the study of the explanations preceding each set of problems and the solving of enough problems to insure a good understanding of them. Do not let later calculations be a burden to you when reference to this chapter would help you very quickly.

Many students solve problems in a very untidy way, covering sheets of paper with figures in a helter-skelter fashion, with no words or labels. The result is that the figures have no meaning after a few hours. If a figure has any meaning or designates some definite thing, it should be labeled. Many times it is necessary to check over a calculation or to answer questions connected with it. This can be done much more easily and quickly if the calculations are in neat order and the figures labeled. If you use the following problems to familiarize yourself with chemical calculations you will find that you will work faster and more efficiently in the laboratory and will better understand what you are doing.

These problems are divided into two main sections, those dealing with simple mathematical operations (percentages and proportions), and those dealing with typical calculations used in elementary chemistry (equations, equivalent weights, titrations, yields of products, etc.).

When solving problems dealing with textile chemistry, you should make free use of the definitions in the Glossary (page 373) in order to recall concepts that you may have forgotten. Table 1, of units and conversions, will be found very useful.

TABLE 1

PHYSICAL UNITS AND CONVERSION FACTORS

Length

1 meter = 100 centimeters
1 centimeter = 10 millimeters
1 millimeter = 1000 microns
1 yard = 3 feet
1 foot = 12 inches

1 meter = 1.094 yards
1 meter = 39.37 inches
1 centimeter = 0.3937 inch
1 micron = 0.000039 inch

1 yard = 0.9144 meter
1 yard = 91.44 centimeters
1 inch = 2.54 centimeters
1 inch = 25.4 millimeters
1 inch = 25,400 microns

Volume

1 liter = 1000 milliliters
1 liter = 1000.027 cubic centimeters
1 gallon = 4 quarts
1 quart = 32 ounces
1 gallon = 231 cubic inches

1 liter = 0.2642 gallon
1 liter = 1.057 quarts
1 liter = 33.815 ounces
1 gallon = 3.785 liters
1 quart = 0.946 liter
1 ounce = 29.573 milliliters
1 U.S. gallon = 0.8327 British gallon
1 British gallon = 1.201 U.S. gallons
1 cubic inch = 16.387 cubic centimeters

Weight

1 kilogram = 1000 grams
1 gram = 1000 milligrams
1 mole = 1000 millimoles

1 pound = 16 ounces
1 ounce = 437.5 grains
1 pound = 7000 grains

TABLE 1—*Continued*

PHYSICAL UNITS AND CONVERSION FACTORS

Weight

1 kilogram = 2.2046 pounds
1 kilogram = 35.274 ounces (avoirdupois)
1 gram = 0.03527 ounce (avoirdupois)

1 pound = 0.4536 kilogram
1 pound = 453.6 grams
1 ounce = 28.35 grams

Area

1 square meter = 10,000 square centimeters
1 square yard = 1296 square inches
1 square foot = 144 square inches

1 square centimeter = 0.155 square inch
1 square inch = 6.452 square centimeters

Temperature

$$°\mathrm{C} = \tfrac{5}{9}(°\mathrm{F} - 32)$$
$$°\mathrm{F} = \tfrac{9}{5}(°\mathrm{C} + 32)$$

Density of Solutions

The relations among the three common methods for expressing the density of solutions (specific gravity, degrees Baumé, Twaddell) are shown below.

$$\text{sp gr} = \frac{145}{145 - °\text{Bé}}$$

$$°\text{Bé} = 145 - \frac{145}{\text{sp gr}}$$

$$\text{sp gr} = 0.005(°\text{Tw}) + 1$$

$$°\text{Tw} = 200(\text{sp gr} - 1)$$

$$\text{per cent by weight} = \frac{\text{gm per liter}}{10(\text{sp gr})}$$

$$\text{pounds per gallon} = \text{gm per liter} \times 0.008345$$

Problems Involving Simple Mathematical Operations

PERCENTAGES

The expression per cent is derived from the Latin *per centum,* which means per hundred, and when used in its ordinary sense means parts per hundred. Obviously the parts must be expressed in the same units, that is, grams per hundred grams, or milliliters per hundred milliliters, or pounds per hundred pounds, etc. If a shipment of wool is found to contain 9% moisture, then 100 gm of it will contain 9 gm of water, or 100 lb of it will contain 9 lb of water (9 parts per 100). If a mixture of alcohol and water contains 40% alcohol by volume, then each 100 liters of it will contain 40 liters of alcohol, or each 100 gal will contain 40 gal of alcohol. Another way to look at percentages is to consider them as hundredths; that is, 40 hundredths of the preceding alcohol-water mixture is alcohol, no matter what total volume is being considered. For example, if we have 3 liters of this mixture, 40 hundredths (or 0.40) of it is alcohol (1.2 liters). When a percentage is thought of as a per cent of something it is always in terms of hundredths.

The calculation of a percentage is quite simple. Only two figures are necessary. One of them is a part and the other is the whole. All that is necessary is to find out how many parts there are for every 100 parts of the whole. The actual procedure is to divide the part by the whole and multiply by 100. This simple calculation is all that is needed. For example, if a sample of wool-cotton union weighs 8 gm and is found to contain 5.6 gm of wool, then 5.6 is the part and 8.0 is the whole; that is, 5.6 parts out of every 8 is wool and the rest is cotton, and the percentage of wool in the union is $(5.6 \div 8) \times 100$, which equals 70%. Another example: if 2.5 gm cotton consumes 0.0075 gm oxygen when it is bleached, then 0.0075 is the part and 2.5 is the whole, and the percentage of oxygen consumed is $(0.0075 \div 2.5) \times 100$, which equals 0.3%. Another example: a test sample of raw wool weighing 5 gm is scoured, rinsed, and dried and is then found to weigh 2 gm. The amount of scouring loss is obviously 3 gm; that is, 3 parts out of every 5 is lost when the wool is scoured. Three is the part and 5 is the whole, and the percentage of scouring loss is $(3 \div 5) \times 100$, which equals 60%. The other 40% is clean wool, and therefore 100 lb of this raw wool would yield 40 lb clean wool. Another example: a sample of cotton cloth 1 yd long (warp length) is treated with a solution of NaOH, washed and dried, and measured again. The new length is 28 in. The original length was 36 in., and therefore the shrinkage is 8 in.; that is, for every 36 in. of this cloth treated in this particular way there will be a shrinkage of 8 in. Thus 8 is the part and 36 is the whole, and the percentage of shrinkage is $(8 \div 36) \times 100$, which is 22.2% shrinkage.

The following problems deal with percentages.

1. A 5-gm sample of raw wool loses 1.5 gm when it is scoured. What is the per cent of scouring loss? *Ans.* 30%.

2. A batch of merino wool shows a scouring loss of 65%. How much clean, scoured wool will be left after 275 lb of this wool is scoured? *Ans.* 96.25 lb.

3. The original breaking strength of a muslin is 65 lb for a 1-in. strip. A certain treatment causes it to lose 12% of its strength. What is the tensile strength after this treatment? *Ans.* 57.2 lb.

4. A sample of weighted silk is found to contain 13% nitrogen. How much nitrogen will be found in 9.75 gm of this silk? *Ans.* 1.267 gm.

5. Fifty-five pounds of weighting material are added to 50 lb of silk. What is the per cent weighting in the weighted silk? *Ans.* 52.38%.

6. A skein of cotton yarn, 12 yd long, is treated with a 23% NaOH solution, washed, dried, and measured. Its length is 9.7 yd. What is the per cent of shrinkage? *Ans.* 19.17%.

7. Raw silk contains about 23.5% sericin. How much sericin will be found in 873 lb of raw silk? *Ans.* 205.2 lb.

8. A 2.7-gm sample of a certain fat will absorb 3.2 gm of iodine. Calculate the per cent of iodine absorbed by this fat. *Ans.* 118.5%.

9. In a particular climate bone-dry wool (entirely free from moisture) is found to regain 16% of its weight when exposed to the air. What will be the weight of 700 lb of bone-dry wool after such exposure? *Ans.* 812 lb.

10. A 2-gm sample of cotton cloth is burned and found to leave 0.075 gm ash. What is the per cent of ash in the cotton? *Ans.* 3.75%.

11. Users of textiles are interested in how much yarns will recover after they are stretched; that is, how close to the original length they will be. One method for testing this recovery is to take 1000 cm of the yarn, stretch it until it is 4% longer, hold that position for 5 min, and then release it. If the yarn shrinks to its original length, it has 100% recovery; that is, it has recovered all its extra stretched length. Usually it recovers only a fraction of that length. A certain synthetic yarn was tested in this way, and its length after recovery was found to be 1010 cm. Calculate the per cent of recovery. *Ans.* 75%.

PROPORTIONS

A proportion consists of two parts, each part a ratio, and the two ratios are equal to each other. Since a ratio is the quotient of one magnitude divided by another of the same kind, it can be expressed as a fraction, e.g., 8/4 is a ratio equal to the number 2. This might be the first part of a proportion, and then the second part would be a ratio that is also equal to 2, e.g., 18/9 or 24/12. The first ratio might not be equal to a whole number but it might be 6/4, which is equal to 1.5. Then the second part of the proportion would be a ratio equal to 1.5, e.g., 9/6 or 24/16.

To express these ratios in the form of a proportion we would write

$$8/4 = 24/12 \quad \text{and} \quad 6/4 = 24/16$$

Not only are the two ratios of a proportion equal to each other, but there is another equality there. If the numerator of the first ratio is multiplied by the denominator of the second ratio, it will equal the product of the numerator of the second ratio and the denominator of the first ratio. If the proportion is $8/4 = 24/12$, then $8 \times 12 = 4 \times 24$.

A ratio need not necessarily be expressed as a fraction; i.e., in place of 8/4 we may write $8 : 4$, and then the preceding proportion would be written $8 : 4 = 24 : 12$. The other equality in this case is found by multiplying the two "extremes" by the two "means," when it will be found that these two products are equal to each other; $8 \times 12 = 4 \times 24$.

Whether the proportion is written $8/4 = 24/12$ or $8 : 4 = 24 : 12$, it will be seen that it contains four numbers. The mathematical value of a proportion lies in the fact that, if any three of the numbers are known, the fourth one can be calculated.

When we leave the realm of pure numbers we must be careful about arranging the four figures in a proportion. Recall that a ratio is a fraction in which the numerator and denominator are magnitudes of the same kind. That is, they may be volumes, or weights, or pressures, or rates. It is not necessary that the two ratios have the same kind of values, for one ratio may be volumes, vol_1 and vol_2, and the other may be grams, gm_1 and gm_2, and the proportion may be written $vol_1 : vol_2 = gm_1 : gm_2$.

When we use proportions in calculations in chemistry, we prefer the second form, $A : B = C : D$, because in many cases it will read like a story and have more meaning than just four numbers. To illustrate this, let us take the reaction between HCl and NaOH. The chemical equation and the molecular weights of the reacting compounds tell us that 36.5 gm HCl will react with 40 gm NaOH. Suppose we wish to know how much NaOH will react with 10 gm HCl. The best way to set up the proportion is

$$36.5 : 40 = 10 : X$$

from which

$$36.5X = 400$$

and

$$X = 10.93 \text{ gm} \qquad (1)$$

Since all four values are in grams, the proportion might just as well be written $36.5 : 10 = 40 : X$, but when written as above ($36.5 : 40 = 10 : X$) it tells a story. Read it. It says if 36.5 gm HCl react with 40 gm NaOH, then 10 gm HCl will react with X gm NaOH.

In this example, the four values are all the same, grams, but suppose they are different, as is the case with the volume of a gas at different temperatures. Recall that the volume of a gas varies directly with the absolute temperature. That is, the higher the temperature, the larger the volume of a gas. If we have 400 cc of gas at 273° A, what will the volume be at 300° A? The volumes must be put on one side of the proportion and the temperatures on the other side.

$$400 : X = 273 : 300$$

from which

$$X = 440 \text{ cc} \qquad (2)$$

This can be expressed in a general way by the proportion $V_1 : V_2 = T_1 : T_2$.

All the proportions discussed thus far have been direct proportions. Now let us look at indirect proportions, where magnitudes vary inversely with each other. A good example is the change of the volume of gas with pressure. You know that when more pressure is put on a gas the volume becomes smaller. This is an inverse or indirect variation: the greater, the smaller.

If we have 400 cc of a gas at 760 mm pressure, what will the volume be at 500 mm pressure? We must put the volumes on one side of the proportion and the pressures on the other side, but the arrangement must be inverse instead of direct; that is, it must conform to $V_1 : V_2 = P_2 : P_1$. The indirect proportion will be

$$400 : X = 500 : 760$$

from which

$$X = 608 \text{ cc} \qquad (3)$$

We have said that the magnitudes in each of the two ratios of a proportion are of the same kind or type (grams over grams), but this is not an absolute requirement, so that very often it is more logical not to adhere to this rule. Refer to example 1 and note that all the values are grams. Note further that those on the left side are theoretical values (standard or equation values), and those on the right side are practical or laboratory values. Now refer to examples 2 and 3. Note that each side of these proportions contains the same kind of magnitudes, volumes on the left and either temperature or pressure on the right. There is another way to arrange these values. Let us put the existing values on one side and the "to be found" values on the other side, and then solve the proportion for the unknown value. In example 2 we have written $400 : X = 273 : 300$, in which volumes are on the left and temperatures are on the right. The existing values among these four are 400 cc and 273°. The "to be found" values (or those under a different set of conditions) are X cc and 300°. Now let us arrange these as suggested above.

$$400 : 273 = X : 300$$

$$X = 440 \text{ cc}$$

This will read like a story: "If the volume is 400 cc at 273° C, then it will be X cc at 300° C."

Note carefully that this method is not applicable to inverse or indirect proportions, and so it cannot be applied to example 3.

The best way to proceed with a problem involving proportions is as follows: Decide whether it is direct or indirect (the larger the larger, or the larger the smaller). If it is a direct proportion, you have a choice. You may put values of the same kind on each side, or you may divide the values into theoretical and practical, or existing and "to be found." If it is an indirect proportion, put the same kind of values in each ratio.

The following problems will help you to understand how to set up proportions.

12. Given 800 cc CO_2 at 300° A, what volume will it occupy at 410° A? *Ans.* 1093.3 cc.

13. Given 700 cc H_2 at 750 mm pressure, what volume will it occupy at 900 mm pressure? *Ans.* 583.3 cc.

14. It is known that 49 gm H_2SO_4 will neutralize 56 gm KOH. How much H_2SO_4 will neutralize 40 gm KOH? *Ans.* 35 gm.

15. How much KOH will be required to react with 45 gm H_2SO_4? *Ans.* 51.5 gm.

16. John drives 50 miles per hour and Joe drives 42 miles per hour. If John gets from here to there in 3 hours, how long will it take Joe? *Ans.* 3.6 hr.

17. If 2.24 liters of CO_2 at 0° C and 760 mm pressure weigh 4.4 gm, what volume will 7.4 gm CO_2 occupy at 0° C and 760 mm pressure? *Ans.* 3.77 liters.

18. What pressure will be required to keep 10 gm CO_2 in a volume of 1.5 liters at 0° C? *Ans.* 2584 mm.

19. How many milliliters are there in 0.357 liter? *Ans.* 357 ml.

20. How many liters are there in 2375 ml? *Ans.* 2.375 liters.

21. What fraction of a liter is 45 ml? *Ans.* 0.045.

22. How many milliliters are there in 2.138 liters? *Ans.* 2138 ml.

23. If 1 liter of NaCl solution contains 5 gm NaCl, how much NaCl will there be in 10 ml? *Ans.* 0.05 gm.

24. Fifty milliliters is what per cent of a liter? *Ans.* 5%.

25. How many grams are in 1.83 lb? *Ans.* 830 gm.

26. How many pounds are in 43 gm? *Ans.* 0.0959 lb.

27. How many gallons are in 2.43 liters? *Ans.* 0.642 gal.

28. Twenty-eight hundred milliliters will make how many gallons? *Ans.* 0.74 gal.

29. What is the Fahrenheit equivalent of 60° C? *Ans.* 140° F.

Problems Dealing with Simple Chemical Calculations

MOLECULAR WEIGHTS (MOLES)

The gram-molecular weight of a compound is the sum of the atomic weights of all the elements in the compound. This weight of a substance is known as 1 mole; half this weight would be 0.5 mole, etc.

30. Calculate the molecular weights of $HC_2H_3O_2$, $C_6H_{12}O_6$, $C_6H_5NH_2$, C_3H_7COOH, $Al_2(SO_4)_3$.

31. How many moles of CH_3COOH are there in 138 gm? *Ans.* 2.3 moles.

32. If you weigh out 35 gm sugar, $C_{12}H_{22}O_{11}$, how many moles will you have? *Ans.* 0.102 mole.

33. How many grams NaCl would you weigh out in order to get 0.35 mole of it? *Ans.* 20.48 gm.

34. One liter of $Ca(OCl)_2$ (bleach liquor) contains 8 gm. How many moles are in this solution? *Ans.* 0.056 mole.

35. Forty grams of NH_4Cl and 25 gm Na_2SO_4 are mixed. What is the total number of moles in this mixture? What is the molar per cent of NH_4Cl in this mixture? *Ans.* 0.924 mole; 80.9%.

SPECIFIC GRAVITY

The specific gravity (sp gr) of a liquid or solid is the ratio of the weight of a definite volume of the substance to the weight of an equal volume of water (measured at 4° C). Thus the specific gravity of water is taken as 1.0, and other liquids (or solids) are compared with it. Since the weight of 1 ml of water at 4° C is 1 gm, and since the volume of water does not change very much with small changes in temperature, we can say that the weight of 1 ml water is 1 gm at ordinary temperatures. Then, for all practical purposes we may think of specific gravity simply as the weight of 1 ml of the substance. When we say that the specific gravity of H_2SO_4 is 1.84, we mean that 1 ml of this H_2SO_4 weighs 1.84 gm. Thus, knowing the specific gravity of any liquid or solution we can easily calculate the weight of any given volume of it.

In the textile and other industries it is quite common to check the strength of solutions by means of specific gravity. Bleach liquor, solutions for weighting silk, and solutions for parchmentizing paper are examples of this. Hydrometers are used for this purpose. Hydrometers are of various types and shapes, but in general they are long tubes with a mercury bulb in the bottom and air space above it, and they are provided with a scale that reads in specific gravity. When the hydrometer is placed in a solution or bath, it sinks as far as it will (depending on the specific gravity of the bath), and the point at which the surface of the liquid cuts the scale is the specific gravity of the solution. The results are not very accurate, but they usually satisfy all practical purposes if they are determined at the temperature for which the hydrometer is calibrated.

Some hydrometers are graduated with arbitrary scales, the two most important of which are the Baumé scale and the Twaddell scale. The readings on either of these arbitrary scales can be converted into specific gravity by means of a formula. (See page 3.)

36. A pure liquid has a specific gravity of 1.2. What is the weight of 1 liter of it? *Ans.* 1200 gm.

37. How many milliliters of it would you measure out to get 546 gm? *Ans.* 455 ml.

38. Suppose that the molecular weight of this liquid compound is 63. How many moles would there be in 1 liter of it? *Ans.* 19 moles.

39. If you are directed to use 45 gm H_2SO_4 for some purpose, what volume of concentrated H_2SO_4 would you measure out (sq gr = 1.84)? *Ans.* 24.4 ml.

40. A bleach liquor is made up to 4° Tw. What is the specific gravity of this solution? *Ans.* 1.02.

41. If 86.8 gm NaCl are dissolved in 1 liter of water at room temperature, the volume will increase to 1029 ml. Calculate the specific gravity of the solution. *Ans.* 1.056.

42. The specific gravity of concentrated HCl is 1.2, and it is 40% HCl. How many grams of real HCl are in 1 liter of concentrated HCl? *Ans.* 480 gm.

43. One liter concentrated HNO_3 contains 990 gm HNO_3, the specific gravity of this solution is 1.4134. Calculate the per cent HNO_3 in concentrated HNO_3. *Ans.* 70%.

44. One liter of pure glacial acetic acid weighs 1050 gm. What is its specific gravity? *Ans.* 1.05.

SOLUTIONS

The strength or concentration of most ordinary solutions is expressed either as grams per liter or as per cent of the solute in the solution. In order to calculate any percentage we must know the weight of the part and the weight of the whole. Therefore in order to calculate the per cent solute in a solution we must know the weight of solute in some definite weight of solution. This involves the specific gravity of the solution, from which the total weight of solution may be determined. When the concentration of the solution is to be expressed in grams per liter, we do not have to know the specific gravity of the solution, but only that a definite volume of the solution contains a certain weight of dissolved substance.

If we know the grams in 1 liter, $\frac{1}{10}$ of this amount will be the grams per 100 ml. We know that parts per hundred is per cent, and, therefore, the grams of solute per 100 ml of solution would be the per cent solute in the solution. However this is true only if the 100 ml of solution weighs 100 gm. This is never precisely true, and yet if we are working with dilute solutions it is not far from true and we may say that the grams per 100 ml is the same as the per cent.

To illustrate how this changes as we go from dilute to more concentrated solutions, let us look at some NaCl solutions. A 2% solution of NaCl really contains 2.02 gm NaCl per 100 ml solution; a 4% solution contains 4.11 gm NaCl per 100 ml; a 10% solution contains 10.7 gm; and a 20% solution contains 23 gm.

If the concentration of the solution is less than 10%, we may use the two systems for expressing concentrations interchangeably. That is, grams per 100 ml will be the same as per cent. Remember that this is not strictly true, but the error is not large enough to be of much importance. However, with more concentrated solutions this cannot be done, and you must be careful to designate clearly the manner of expressing concentrations.

The Concentration of Laboratory Reagents

In all chemical laboratories the common inorganic acids and bases are made up to have a fairly definite concentration. These reagents are used in all laboratory procedures when dilute acid is required, or when any acid or base is mentioned without any qualifying statement about its concentration. These solutions are labeled "Reagent."

It is very convenient to know how concentrated these reagents are because they may be used for making more dilute solutions. For example, if you wish to make a 5% solution of HNO_3, you could start with reagent HNO_3 and dilute it with the proper amount of water. In a course in textile chemistry you will have to do this very often, and it is therefore essential that you know how strong these reagents are. Knowing how they are made up, you can calculate their concentration. This information is given in the accompanying chart. Make the proper calculations and fill in the blank spaces. You will refer to this chart many times.

In the first column you will find the quite abbreviated directions by which the reagents are made up: that is, what the starting material is and how much it is diluted in order to make the reagent. In the second column you will find the concentration of each starting material. In the third column you will find the specific gravities of the reagents. Calculate the concentration of each reagent in grams per liter, and enter these figures in the fourth column. These values can be calculated from the information given in the first two columns. Knowing the number of grams of acid or base in each liter and the specific gravity of the reagent,

THE REAGENT ACIDS AND BASES

Starting Material and Method for Making the Reagent	Weight of Starting Material per Liter	Specific Gravity of Reagent	Concentration of Reagent in	
			grams/liter	per cent
1.1 liters concentrated H_2SO_4 made up to 8 liters reagent	1760 gm	1.152		
7.5 liters concentrated HNO_3 made up to 40 liters	990 gm	1.098		
5 liters glacial acetic acid made up to 20 liters	1000 gm	1.034		
15 lb solid NaOH made up to 40 liters		1.165		
17.5 liters concentrated NH_4OH made up to 40 liters	640 gm NH_4OH	0.944		
12.5 liters concentrated HCl made up to 40 liters	Concentrated HCl, specific gravity 1.2, is a 40% solution	1.068		

you can calculate the strength of each solution in terms of per cent. Enter these figures in the last column.

These calculations may be made outside the classroom after you are sure you understand how to use the table. You will use this information many times during your textile chemistry course, and so you must be sure that your calculations are correct. Have them checked.

45. How would you make a 12% solution of sugar? a 9.5% solution of salt? a 2.3% solution of soap?

46. How would you make a solution of sugar which would contain 47 gm/l? Each milliliter of this solution would contain how much sugar?

DILUTION OF SOLUTIONS

It is often convenient and necessary to make a solution of a definite concentration by diluting a more concentrated solution. You will do this frequently, starting with a "reagent" and diluting it to some smaller concentration. This involves an inverse proportion. Suppose that you have a solution of NaCl that contains 10 gm/l, and you wish to make one that contains 2 gm/l. It is obvious that the latter solution is 1/5 as concentrated, or 5 times as dilute, as the former solution, and in order to make it you would dilute the more concentrated solution five times. But suppose you start with a solution that contains 17.3 gm/l and wish to make one with 3.9 gm/l. In this case a proportion must be used. The proportion will have two kinds of values, grams per liter and volumes, and these values for the two solutions are inversely proportional to each other. That is, the larger the volume, the fewer grams per liter there are. Therefore, you must select one volume, either the volume you wish to make or the volume of the starting solution you wish to use, and give it a definite value. For example, start with 100 ml of the more concentrated solution and calculate the volume it will have when it has been diluted to the proper amount. The two volumes must be on one side of the proportion and the two weights on the other side, and it must be an inverse proportion, i.e., it must be $V_1 : V_2 = \text{gm}_2 : \text{gm}_1$. Therefore

$$100 : X = 3.9 : 17.3$$

from which

$$X = 443.6 \text{ ml}$$

Thus, in order to make this solution you would measure out 100 ml of the 17.3 gm/l solution and add enough water to make 443.6 ml.

If you wish to make a definite volume of dilute solution, then V_2 has a fixed value, and V_1 is the one to be calculated. You can determine all possible relations among volumes and weights per volume by means of this inverse proportion.

The diluting of a solution from a higher to a lower per cent is not so simple, unless both solutions are less than 10%. Recall that in such dilute solutions the gm/100 ml may be considered the same as the per cent concentration, i.e., 4 gm/100 ml is the same as a 4% solution. With more concentrated solutions the error involved becomes quite large. If you wish to dilute a solution from 8% to 1.5%, you may do it by means of inverse proportion as explained above, but if the dilution is to be from 25% to 1.5% this simpler method cannot be used. This is because the specific gravity must be taken into consideration.

Let us take 1 liter of reagent HNO_3 and dilute it to a 1.5% solution. The reagent is a 17.8% solution with a specific gravity of 1.098. Therefore, the weight of the 1 liter is 1098 gm, and 17.8% of this weight is the weight of HNO_3 contained in the 1 liter. This is 186 gm, the weight of real HNO_3 in each liter of the reagent. Since per cent is the part divided by the whole times 100, we must know the weight of HNO_3 in the diluted solution and also the specific gravity of the diluted solution, in order to calculate its total weight. No matter how much the 1 liter of reagent HNO_3 is diluted, the weight of HNO_3 remains 186 gm, but the specific gravity becomes smaller. The equation for this calculation is

$$\frac{186\text{ gm} \times 100}{\text{total weight of dilute solution}} = 1.5\%,$$

from which

$$\text{total weight of dilute solution} = \frac{18{,}600}{1.5} = 12{,}400\text{ gm}$$

Of the 12,400 gm (the weight of the 1.5% solution to be made) 1098 gm came from the 1 liter of reagent HNO_3 and the remainder of the 12,400 gm is the weight of water to be added to make the 1.5% solution. This difference is 11,302 gm. Therefore, if 11,302 gm of water are added to 1 liter of reagent HNO_3, the result will be a 1.5% HNO_3 solution. The weight of it will be 12,400 gm.

47. How would you make 3.5 liters of a 4% sugar solution?

48. If 485 ml of NaCl solution contains 54 gm NaCl, how would you label the solution in gm/ml? *Ans.* 0.11 gm/ml.

49. The specific gravity of concentrated H_2SO_4 is 1.84. One liter of it contains 1760 gm H_2SO_4. Calculate the per cent of H_2SO_4 in concentrated H_2SO_4. *Ans.* 97.5%.

50. Starting with concentrated H_2SO_4, how could you make a 3% solution?

51. A 30% K_2CrO_4 solution has a specific gravity of 1.28. How many grams K_2CrO_4 are in 1 liter of it? *Ans.* 384 gm.

52. A solution of soda ash contains 6 gm/l. How much of it would you measure out to get 0.57 gm soda ash? *Ans.* 95 ml.

53. The specific gravity of 21% NaCl solution is 1.16. How much would you measure out to get 3.5 gm NaCl? *Ans.* 14.3 ml.

54. If 4.7 gm salt are dissolved in 1560 ml water, what is the per cent of salt in solution? *Ans.* 3.01%.

55. How much NaOH is there in 157 ml of a 4.5% solution? *Ans.* 7.06 gm.

56. Eight grams NaCl are dissolved in 180 ml water. Assuming there is no change in volume, calculate the specific gravity of the solution.

Ans. 1.044.

57. What is the measurement in grams per liter of a solution that is 4.7% solute?

58. A 20% HCl solution has a specific gravity of 1.098. What volume of concentrated HCl would you measure out (and dilute to 1 liter) to make this solution? Concentrated HCl is a 40% solution with a specific gravity of 1.2.

Ans. 457.5 ml.

59. One liter of an NH_4Cl solution containing 192.6 gm has a specific gravity of 1.07. Calculate the difference between the per cent solution based on gm/100 and on specific gravity.

STOICHIOMETRIC CALCULATIONS

Stoichiometry is a branch of chemistry dealing with the molecular proportions in which compounds react. A stoichiometric equation is one that is properly balanced and that shows the molar quantities of reactants and resultants. Knowing the number of moles of reacting substances (as defined by the stoichiometric equation), together with their molecular weights, you can calculate the theoretical yield of all products in terms of moles or grams.

In these calculations direct proportions are used. For example, the stoichiometric equation for the reaction between H_2SO_4 and NaOH is

$$\underset{98}{H_2SO_4} + \underset{2\times 40}{2NaOH} \longrightarrow \underset{142}{Na_2SO_4} + \underset{2\times 18}{2HOH}$$

This equation tells you the number of moles of reactants and resultants, and also the weight of each. You can use these stoichiometric values for calculations involving reactions of molecules, e.g., the number of moles of Na_2SO_4 produced by the action of an excess of H_2SO_4 on 0.4 mole NaOH. The story is "if 2 moles NaOH will make 1 mole Na_2SO_4, then 0.4 mole NaOH will make X moles Na_2SO_4." Put these figures into a direct proportion

$$2 : 1 = 0.4 : X$$

from which $X = 0.2$ mole Na_2SO_4.

Perhaps the more important calculations are those involving weights of reactants and resultants. The numbers below the formulas in the preceding equation are the molecular weights of the compounds. Suppose you wish to know the weight of Na_2SO_4 that will be produced by the action of H_2SO_4 on 48 gm NaOH. The equation tells you that 80 gm NaOH will make 142 gm

Na_2SO_4. These are the figures for one side of a direct proportion. The "to be found" values go on the other side.

$$80 : 142 = 48 : X$$
$$X = 85.2 \text{ gm } NaSO_4$$

In such a manner the weight of any compound formed or required for a chemical reaction can be calculated.

60. What weight of H_2SO_4 will be required to make 14 gm Na_2SO_4? *Ans.* 9.1 gm.

61. When HCl reacts with NaOH, how much NaCl will be made from 28 gm HCl? *Ans.* 44.9 gm.

62. If you measure out 50 ml concentrated H_2SO_4 (97.5%) (sp gr = 1.84) and treat it with an excess of NaOH, how much Na_2SO_4 will be formed? *Ans.* 130 gm.

63. How much KOH will be required to react with 75 gm of the fatty acid $C_{11}H_{23}COOH$? *Ans.* 21 gm.

64. When $Ca(OH)_2$ reacts with 60 gm HCl, how much $CaCl_2$ will be formed? *Ans.* 91.2 gm.

65. Measure out 200 ml Na_2CO_3 solution (10 gm/l), and add an excess of HCl. What weight of NaCl will be formed? *Ans.* 2.2 gm.

2 · Organic Chemistry

With the exception of glass and asbestos, all textile fibers used for weaving, knitting, and stuffing are organic in nature. All of them are products of organic reactions taking place in nature or by the hand of man, and all of them may be considered synthetic fibers. Nature synthesizes such fibers as cotton, wool, and silk, and man synthesizes such fibers as nylon, acetate rayon, and vinyon. It is therefore axiomatic that the improvement of old processes and the development of new ones in the textile industry, the maintenance of fabrics made from natural fibers, and the synthesis of new man-made fibers all depend on an exact knowledge of the constitution and properties of organic compounds and an understanding of organic reactions. These are important tools of the textile technologist, and they should be equally important to the buyer, consumer, and teacher of textiles.

The purpose of this chapter is to discuss organic chemistry in a concise, concentrated, but elementary way, emphasizing those families of compounds and reactions that play important parts in the textile industry. If the reader wishes to extend this discussion in any special field, he may consult any of the large number of textbooks on organic chemistry that are available.

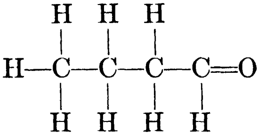
After a brief introduction we shall discuss the following families of organic compounds: hydrocarbons, alcohols, aldehydes and ketones, acids, esters, amines, amides, amino acids, fats, proteins, and carbohydrates. The pattern of the discussion will be the same for each family: (*a*) structural formulas and names, (*b*) methods of preparation, and (*c*) physical and chemical properties.

We have found that one of the biggest stumbling blocks and causes of confusion is the lack of a clear vocabulary. It is just as necessary to learn this technical vocabulary as it is to know the meaning of the words used in ordinary conversation. This matter of vocabulary should be kept in mind while reading this chapter. If necessary, make use of the glossary near the end of the book.

Organic chemistry was formerly considered to be the study of those chemical compounds that were produced as a result of some vital process, but so many of them have been synthesized in the laboratory and could not be made by any plant or animal that we now think of organic chemistry as the study of compounds containing carbon. All organic compounds contain carbon together with only a few other elements such as hydrogen, oxygen, nitrogen, the halogens, and sulfur. This does not add up to very many elements, and yet over 450,000 organic compounds are known. This is not so strange, after all, when we realize that we can take a very few types of building materials and construct an almost unlimited number of houses. Why should not nature take a few elements and make all these thousands of compounds? All these houses differ from each other only in a very few things—the kind of structural elements, the number of them, and their arrangement with respect to each other. Thus we have small houses, large houses, conveniently arranged houses and inconvenient ones, houses with wood shingles or asphalt shingles, with steam or hot-air heat. The large number of organic compounds is analogous to this. We may have $C_8H_{10}O_3N_2$, and these 23 atoms could arrange themselves in many ways to form many compounds. On the other hand, we might have many smaller compounds such as C_2H_5OH, or some compounds might be large but have no N or O in them.

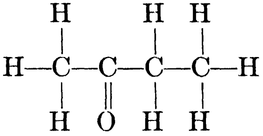
The first thing we learn about organic compounds is that they differ from each other not only in the number of elements in the molecule but also in the arrangement of these elements. The organic chemist thinks this matter of arrangement so important that he draws pictures of the compounds (floor plans of the houses) to show the positions occupied by all the elements. These formulas are known as *structural formulas*, and they are abbreviated ways for expressing the behavior of a compound. It is apparent that the chemical behavior of a substance is the reason for its being used (or not used) for some special purpose, and therefore the functional part of that compound is very important. Perhaps only a small portion of the molecule reacts and the rest of the molecule remains unchanged. It is with these reactive fragments that we are concerned, and they are emphasized by the use of structural formulas.

To illustrate the use of structural formulas let us take two compounds having the same molecular formula C_4H_8O. A study of their properties shows that they have the following structures:



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C{=}O \\ & & | & & | & & | & & | \\ & & H & & H & & H & & H \end{array}$$

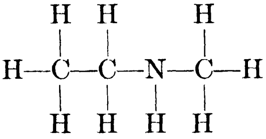
and



$$\begin{array}{ccccccccccc} & & H & & & & H & & H & & \\ & & | & & & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & \| & & | & & | & & \\ & & H & & O & & H & & H & & \end{array}$$

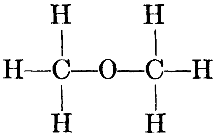
The functional part of these compounds is where the oxygen is, and it is clear that they will behave differently, because the oxygen is in two different places.

These two structural formulas illustrate a very fundamental thing about organic compounds. They are made up of a skeleton chain of atoms (in this case a chain of four carbons) to which other atoms are attached, and the arrangement is such that each carbon has a valence of 4. We shall find some skeletons with other elements in them, such as



$$\begin{array}{ccccccccccc} & & H & & H & & & & H & & \\ & & | & & | & & & & | & & \\ H & - & C & - & C & - & N & - & C & - & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$

and



$$\begin{array}{ccccccccc} & & H & & & & H & & \\ & & | & & & & | & & \\ H & - & C & - & O & - & C & - & H \\ & & | & & & & | & & \\ & & H & & & & H & & \end{array}$$

These cumbersome structural formulas can be condensed to a form that is more compact and easier to write and read. The condensed structural formulas for the preceding four compounds are shown below.

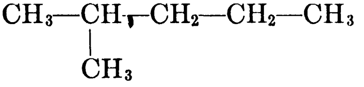
$CH_3{-}CH_2{-}CH_2{-}CHO$ $CH_3{-}CO{-}CH_2{-}CH_3$
$CH_3{-}CH_2{-}NH{-}CH_3$ $CH_3{-}O{-}CH_3$

HYDROCARBONS

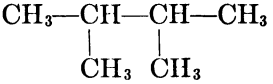
Hydrocarbons, as the word indicates, are compounds composed of only carbon and hydrogen. They may be divided into two large groups, the aliphatic hydrocarbons and the aromatic hydrocarbons. Many of the aliphatic hydrocarbons are found in crude petroleum, and some of the aromatic ones are found in the coal tar obtained by the distillation of coal.

Most aliphatic hydrocarbons have open-chain structures, either long continuous chains or chains with forks in them, such as

$CH_3—CH_2—CH_2—CH_2—CH_2—CH_3$ (hexane)



$CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_2—CH_2—CH_3$ (2-methylpentane)



$CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_3$ (2,3-dimethylbutane)

The textile chemist is interested in these open-chain structures. They are subdivided into saturated and unsaturated hydrocarbons, that is, those having only single bonds between carbons and those in which some carbons are joined by either double or triple bonds. To the first group belong the paraffin hydrocarbons, and to the second group the olefins and acetylenes.

All the aromatic hydrocarbons have ring structures, the most important of which is the benzene ring, and most aromatic compounds may be considered derivatives of benzene. These will be discussed later.

THE PARAFFIN HYDROCARBONS

The general formula for the paraffins is C_nH_{2n+2}; that is, the number of hydrogens in a paraffin is twice the number of carbons plus 2, e.g., CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}. They form a series of compounds, each member of which differs from its neighbor by CH_2. Such a series is known as an *homologous series.*

Another way to write the general formula is RH. The letter R is a symbol used to designate an *alkyl group.* It is evident that an alkyl group is a combination of carbons and hydrogens having one less hydrogen than the paraffin, and a general formula C_nN_{2n+1}. It is not a compound or a molecule, but only a part of a compound or molecule having a valence of 1. These alkyl groups occur in practically all organic formulas (and general formulas), and their formulas and names must be learned at once. The names and formulas of the paraffin hydrocarbons and their respective alkyl groups are shown in Table 2.

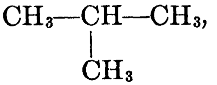
The formulas in the second column are known as molecular formulas, which means that they tell us the number of atoms in the compound and its molecular weight, and that is all. However, we find that, beginning with butane, the paraffins exist in

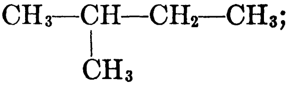
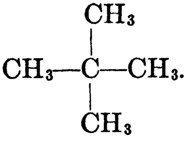
TABLE 2

THE PARAFFIN HYDROCARBONS

Paraffin	Formula	Alkyl	Formula
Methane	CH_4	Methyl	CH_3
Ethane	C_2H_6	Ethyl	C_2H_5
Propane	C_3H_8	Propyl	C_3H_7
Butane	C_4H_{10}	Butyl	C_4H_9
Pentane	C_5H_{12}	Pentyl	C_5H_{11}
Hexane	C_6H_{14}	Hexyl	C_6H_{13}
Heptane	C_7H_{16}	Heptyl	C_7H_{15}
Octane	C_8H_{18}	Octyl	C_8H_{17}
Nonane	C_9H_{20}	Nonyl	C_9H_{19}
Decane	$C_{10}H_{22}$	Decyl	$C_{10}H_{21}$

two or more isomeric forms. For example, there are two butanes, one boiling at −0.6° C and the other at −11.8° C. Butane exhibits what is known as structural isomerism, that is, it can exist in two isomeric forms, and these two forms are said to be isomeric with each other. The most logical conclusion that we can draw from this is that the atoms of carbon and hydrogen must be arranged differently in the two butanes, and since they are actually different compounds they must be given different names.

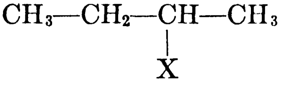
We apply the name normal to compounds in which the carbons are arranged in straight chains, and so normal butane is $CH_3—CH_2—CH_2—CH_3$. But the same atoms can be arranged differently, i.e.,  $\underset{\textstyle CH_3}{CH_3—\underset{|}{CH}—CH_3}$, and this compound is called isobutane, or 2-methyl propane. The latter name means that a methyl group, CH_3, has been substituted for one of the hydrogens of propane attached to carbon atom 2.

Pentane can exist in three isomeric structures:
normal pentane, $CH_3—CH_2—CH_2—CH_2—CH_3$;
isopentane (or 2-methylbutane),  $CH_3—\underset{\underset{\textstyle CH_3}{|}}{CH}—CH_2—CH_3$;
and neopentane (or 2,2-dimethylpropane),  $CH_3—\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}—CH_3$.

Since alkyl groups are the same as paraffins minus one hydrogen, and since the higher paraffins can exist in various isomeric forms, the alkyl groups must also exist in more than one form. If one hydrogen is taken from a paraffin it will leave a free valence bond that can hold something else, such as Cl, OH, or NH_2. In the following formulas X will represent such groups. Let us take the butyl group, C_4H_9, and show how it can have four structures.

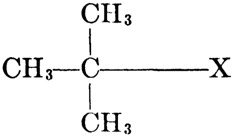
$$CH_3—CH_2—CH_2—CH_2—X$$

(normal butyl X)



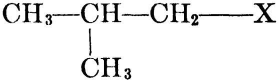
$$CH_3—CH_2—\underset{\displaystyle X}{\underset{|}{CH}}—CH_3$$

(secondary butyl X)



$$CH_3—\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}—X$$

(tertiary butyl X)



$$CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_2—X$$

(isobutyl X)

Note the difference among primary, secondary, and tertiary. In the primary arrangement the carbon holding X is attached to only one carbon; in the secondary arrangement the carbon holding X is attached to two other carbons; in the tertiary compound the carbon holding X is attached to three other carbons. The fourth structure looks like a primary because the carbon holding X is attached to only one other carbon, but it is different from the first compound because there is a fork in the chain, and so the prefix "iso" is used.

The names of the isomeric alkyl groups having three, four, and five carbons should be memorized, because they will occur in all the families to be studied.

The paraffin hydrocarbons are obtained by the distillation of petroleum. Gasoline is a mixture of many different and isomeric paraffins having the proper boiling point range. Kerosene likewise is a mixture of a large number of higher-boiling paraffins. Paraffin wax is a mixture of paraffins having 28 or more carbons.

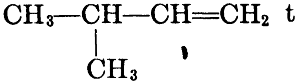
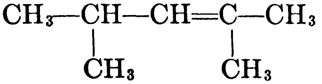
In textile chemistry we are not very much interested in the paraffins, except that the low-boiling ones, such as gasoline, are good solvents for fats and oils, for which reason they may be used for cleaning textile materials and removing grease from them.

The most important chemical property of the paraffins is the reaction with halogens (chlorine and bromine). The reaction is known as substitution; that is, one or more hydrogens are replaced by chlorine or bromine atoms. For example, if ethane gas is passed into bromine, the ethane hydrogens are substituted by bromine, and a mixture of brominated compounds is obtained.

$$\begin{aligned} CH_3{-}CH_3 + Br_2 \longrightarrow\ & CH_3{-}CH_2{-}Br \\ & CH_3{-}CHBr_2 \\ & CH_3{-}CBr_3, \quad \text{etc.} \end{aligned}$$

THE OLEFINS

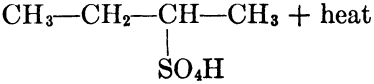
These are hydrocarbons in which two or more carbons are joined by double bonds, which are very reactive, so that all the chemical reactivity of the olefins is tied up with these double bonds. A knowledge of the chemistry of the double bond, not only in olefins but also in other compounds, is interesting to us because the manufacture of all the new synthetic resin fibers (velon, vinyon, etc.) depends upon such double bonds. In Chapter 11 the chemistry of the plastics will be discussed in detail.

The names of the homologous series of olefins are like those of the paraffins except for the ending. Whereas the names of paraffins end in *ane*, the names of olefins end in *ene*. The first part of the name indicates the number of carbons: *meth* means one carbon, *eth* means two carbons, *prop* three, *but* four, etc. Thus the olefin with three carbons is propene, with four carbons is butene, with six is hexene, etc. In olefins with four or more carbons we have a new kind of isomerism, positional isomerism, in which the skeletons of the two isomers are the same but the position of the double bond is different. For example, $CH_3{-}CH_2{-}CH{=}CH_2$ and $CH_3{-}CH{=}CH{-}CH_3$. In naming these two butenes we number the bonds beginning at the end nearest the double bond, so that the number will be the smallest possible. Thus the first butene above will be named 1-butene because the double bond is in position 1. The second butene above will be named 2-butene because the double bond is in the number 2 position. If there are alkyl groups attached to an olefin chain, the compound is named as a substitution product of the double-bond chain. For example, in  $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH=CH_2$ the methyl group is on carbon 3 of 1-butene, and the compound will be named 3-methyl-1-butene. The compound  $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH=\underset{\underset{CH_3}{|}}{C}-CH_3$ will be named 2,4-dimethyl-2-pentene.

Olefins are prepared by splitting off something from a saturated compound by chemical reaction or by pyrolysis (decomposition by heat). If $CH_3-CH_2-CH_2Cl$ is reacted with alcoholic KOH, hydrogen chloride will be split off, the Cl leaving carbon 1 and one H leaving carbon 2, and the product will be $CH_3-CH=CH_2$. An organic compound having halogens on adjacent carbons may be treated with sodium or zinc to split off the two halogens:

$$CH_3-CHBr-CHBr-CH_3 + Zn \longrightarrow CH_3-CH=CH-CH_3 + ZnBr_2$$

The pyrolysis of alkyl hydrogen sulfates will yield olefins:



$$CH_3-CH_2-\underset{\underset{SO_4H}{|}}{CH}-CH_3 + \text{heat} \longrightarrow CH_3-CH=CH-CH_3 + H_2SO_4$$

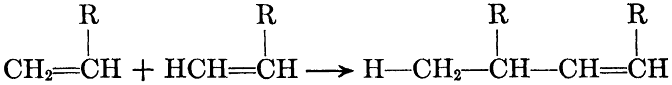
We are not so much interested in how olefins are prepared as we are in what they will do. The most important property of the double bond is addition. When something adds to a double bond, the unsaturated compound is changed into a saturated one, and the double bond becomes a single bond. Thus

$$\begin{aligned}
CH_2=CH_2 + Cl_2 &\longrightarrow CH_2Cl-CH_2Cl\\
CH_2=CH_2 + HBr &\longrightarrow CH_3-CH_2Br\\
CH_2=CH_2 + \underset{\text{(concentrated)}}{H_2SO_4} &\longrightarrow CH_3-CH_2SO_4H
\end{aligned}$$

When an olefin is boiled with alkaline $KMnO_4$ the compound is oxidized; it splits at the double bond and forms two acids.

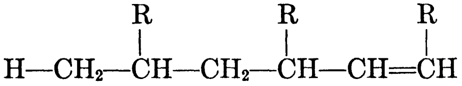
$$C_2H_5-CH=CH-CH_3 \xrightarrow{\text{oxidation}} C_2H_5COOH + CH_3COOH$$

Perhaps the most important property of double bond compounds, as far as textile chemistry is concerned, is that they can be polymerized. Polymerization is a type of organic reaction in which a complex molecule of high molecular weight is produced by the combination of many simple molecules. It is characteristic of unsaturated compounds having double or triple bonds between carbon atoms. When simple linear polymerization takes place one molecule adds to another, e.g.,



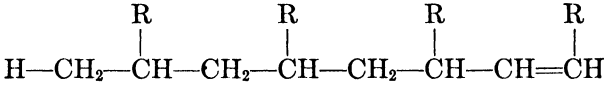
$$CH_2{=}\overset{R}{\overset{|}{C}}H + HCH{=}\overset{R}{\overset{|}{C}}H \longrightarrow H{-}CH_2{-}\overset{R}{\overset{|}{C}}H{-}CH{=}\overset{R}{\overset{|}{C}}H$$

An H from the second molecule adds to the left-hand carbon of the first molecule, and the rest of the second molecule attaches itself to the right-hand carbon of the first molecule. The product is twice as big as the original and is called a *dimer.* Since the dimer has a double bond it may add on a third molecule of olefin and yield

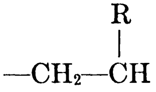


$$H{-}CH_2{-}\overset{R}{\overset{|}{C}}H{-}CH_2{-}\overset{R}{\overset{|}{C}}H{-}CH{=}\overset{R}{\overset{|}{C}}H \quad \text{(a trimer)}$$

The addition of another molecule will give



$$H{-}CH_2{-}\overset{R}{\overset{|}{C}}H{-}CH_2{-}\overset{R}{\overset{|}{C}}H{-}CH_2{-}\overset{R}{\overset{|}{C}}H{-}CH{=}\overset{R}{\overset{|}{C}}H$$



Notice that the fragment $-CH_2{-}\overset{R}{\overset{|}{C}}H$ keeps repeating itself. This process will continue until a polymer of high molecular weight is obtained.

Many organic compounds used in connection with the textile industry contain more than one olefinic double bond. If they have two double bonds they are called dienes and are named by using a syllable indicating the number of carbons in the chain and adding the syllable "diene." This name is preceded by numbers which tell the position of the two double bonds; e.g., $CH_3{-}CH{=}CH{-}CH{=}CH_2$ is 1,3-pentadiene, and $CH_2{=}CH{-}CH_2{-}CH{=}CH_2$ is 1,4-pentadiene. Dienes with double bonds separated by a single bond are said to have a *conjugated system* of double bonds. These systems are quite easily polymerized, and synthetic rubber is made by such a process.

Some ethylene derivatives can be polymerized to form resins, and these resins can be fabricated into plastic fibers that are used in textile materials. Such derivatives are $CH_2{=}CHCl$, vinyl chloride; $CH_2{=}CCl_2$, vinylidene chloride; and $CH_2{=}CHOOC{-}CH_3$, vinyl acetate. The manufacture of fibers from such compounds will be discussed in detail in Chapter 12. It is our purpose at this time merely to point out that compounds containing olefinic double bonds can be polymerized, and that the manufacture of synthetic fibers, based on this reaction, is rapidly changing the picture of the entire textile industry.

THE ACETYLENES

These hydrocarbons contain triple bonds and constitute an homologous series comparable with the paraffins and olefins. However, we are interested in only the first member, acetylene, $HC{\equiv}CH$, which is a gas made by the action of water on calcium carbide,

$$CaC_2 + 2HOH \longrightarrow C_2H_2 + Ca(OH)_2$$

Several reactions of acetylene are definitely connected with textile chemistry. The following are addition reactions in which various compounds will add to acetylene under more or less special conditions.

If acetylene is treated with an excess of HBr it will add two molecules of the HBr

$$HC{\equiv}CH + 2HBr \longrightarrow CH_3{-}CHBr_2$$

It will add two molecules of Br_2

$$HC{\equiv}CH + 2Br_2 \longrightarrow CHBr_2{-}CHBr_2$$

If a mixture of acetylene and hydrogen chloride gas is passed over silica gel coated with a deposit of mercuric chloride at about 30° C, one molecule of HCl will add to C_2H_2.

$$HC{\equiv}CH + HCl \longrightarrow \underset{\text{(vinyl chloride)}}{CH_2{=}CHCl}$$

Vinyl chloride is important in synthetic fiber production. It can also be made by passing acetylene into a hydrochloric acid solution of certain metal chlorides at about 70° C.

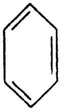
When acetylene gas is passed through acetic acid containing a suspension of finely divided mercuric sulfate at 35° C, one molecule of acetic acid adds to acetylene to form vinyl acetate

$$HC{\equiv}CH + CH_3COOH \longrightarrow CH_2{=}CHOOC{-}CH_3$$

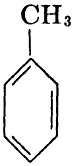
At higher temperatures a diacetate is formed. Mixtures of vinyl chloride and vinyl acetate are used in the manufacture of Vinyon, a new plastic type of yarn. (See page 340.)

THE AROMATIC HYDROCARBONS

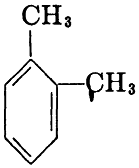
Some of the most important hydrocarbons are derived from coal tar, a by-product obtained in the manufacture of coke and illuminating gas by the pyrogenic decomposition of coal. They include benzene, C_6H_6; toluene, $C_6H_5—CH_3$; xylene, $C_6H_4(CH_3)_2$; and naphthalene, $C_{10}H_8$. All these compounds contain the benzene ring, which consists of six carbons joined together by alternate single and double bonds. In benzene itself each carbon holds one hydrogen. Note the difference between this ring and the cyclic paraffins, olefins, and dienes. Various atoms and groups can be substituted in place of the hydrogens of benzene to give a very large number of aromatic compounds. Many of these compounds have common names, but there is a system for naming them as derivatives of benzene. To do this the benzene carbons are numbered, beginning with any one on which some group has been substituted. Then the carbons holding other groups will have definite numbers. (See below.) Another system for naming aromatic compounds containing two substituents uses the words *ortho*, *meta*, and *para*. If the two substituents are on adjacent carbons (in the 1,2 positions) it is ortho, if they are on the 1,3 carbons they are meta to each other, and the 1,4 positions are para. These systems for naming are shown below. Because the benzene ring is a part of the structural formulas of so many compounds, it is customary to show it in the form of a hexagon having alternate single and double lines. The carbons and hydrogens are not shown, but it is understood that there is a CH group at each corner of the hexagon. When other atoms or groups are substituted on the ring they take the place of one or more hydrogens.



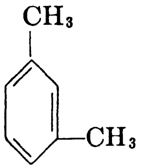
(benzene)



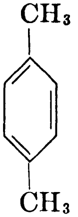
(toluene or methyl benzene)



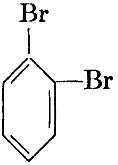
(1,2-dimethylbenzene
or ortho-xylene
or *o*-xylene)



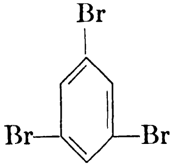
1,3-dimethylbenzene or
meta-xylene or
m-xylene)



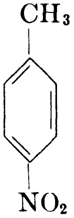
(1,4-dimethylbenzene
or para-xylene
or *p*-xylene)



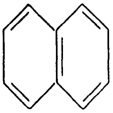
(*o*-dibromobenzene)



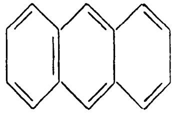
(1,3,5-tribromobenzene)



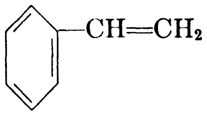
(4-nitrotoluene or
p-nitrotoluene)



(naphthalene)



(anthracene)



(phenylethylene or
styrene)

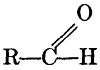
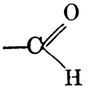
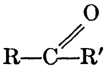
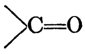
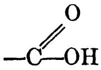
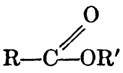
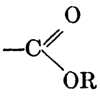
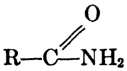
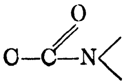
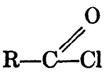
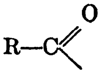
The C_6H_5 group is the phenyl group, and in styrene this group has been substituted in place of one of the hydrogens of ethylene. Styrene is used in making high-polymer resins.

Aromatic hydrocarbons will form substitution products with halogens, nitric acid, sulfuric acid, and with alkyl halides under special conditions. A great number of important compounds can be made from these substitution products, so that, both directly and indirectly, benzene and naphthalene are mother substances of a large number of compounds.

Alcohols

Before taking up a brief study of alcohols it will be advantageous to look at the general structural formulas of some of the other families of organic compounds. Some of the families can be produced from alcohols or may react with alcohols, so it is well to know something of their structures and characteristic groups. In these formulas the letter R means an alkyl group (methyl, ethyl, etc.). Some of these families are arranged in Table 3.

TABLE 3

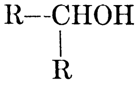
Family	General Formula	Characteristic Group or Skeleton	
Alcohols	ROH	—OH	Alcohol
Aldehydes			Aldehyde
Ketones			Carbonyl
Acids	R—COOH		Carboxyl
Ethers	R—O—R′	C—O—C	Ether
Esters			Ester
Amines	$R—NH_2$	$—NH_2$	Amino
Amides			Amide
Acid chloride			Acyl
Nitriles	R—CN	—CN	Cyan

The third column of the table shows either the characteristic group found in each member of each family, or the specially arranged skeleton which is characteristic of each family. The fourth column names these groups or skeletons.

All aliphatic alcohols conform to the general formula ROH, and they are all known as carbinols, the carbinol carbon atom being the one to which the —OH group is attached. Because of different arrangements of carbons around the carbinol carbon atom, the family of alcohols can be divided into three groups

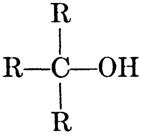
$R—CH_2OH$

(primary alcohol)



$$R—\underset{\displaystyle R}{\underset{|}{C}}HOH$$

(secondary alcohol)



$$R—\underset{\displaystyle R}{\underset{|}{\overset{\displaystyle R}{\overset{|}{C}}}}—OH$$

(tertiary alcohol)

This tells us that all primary alcohols will have the $—CH_2OH$ group in them, all secondary alcohols will have the $—\overset{|}{C}HOH$ group, and the $—\underset{|}{\overset{|}{C}}OH$ group will be found in all tertiary alcohols.

These groups are known as characteristic groups or *functional groups*. If we learn the properties of primary alcohols (how they function), we can then predict these same properties for any compound that contains the $—CH_2OH$ group. Some substances contain more than one kind of alcohol group; e.g., cellulose (cotton) contains both primary and secondary alcohol groups and therefore will behave like a primary alcohol and also like a secondary alcohol.

Alcohols are named by two systems: (1) the name of the alkyl group followed by alcohol, or (2) the syllable telling the number of carbons followed by "anol." CH_3OH is either methyl alcohol or methanol; C_2H_5OH is either ethyl alcohol or ethanol. Propyl alcohol can exist in two isomeric forms, which must be distinguished by two different names.

$CH_3—CH_2—CH_2OH$

(normal propyl alcohol or
primary propyl alcohol or
1-propanol)

$CH_3—CHOH—CH_3$

(isopropyl alcohol or
secondary propyl alcohol or
2-propanol)

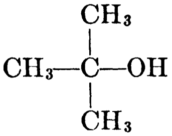
There are four butyl alcohols with the molecular formula C_4H_9OH.

$$CH_3—CH_2—CH_2—CH_2OH$$

(normal butyl alcohol, a primary alcohol, or 1-butanol)

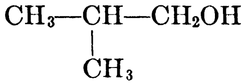
$$CH_3—CH_2—CHOH—CH_3$$

(secondary butyl alcohol or 2-butanol)



$$CH_3—\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}—OH$$

(tertiary butyl alcohol or 2-methyl-2-propanol)



$$CH_3—\underset{\displaystyle CH_3}{CH}—CH_2OH$$

(isobutyl alcohol, a primary alcohol, or 2-methyl-1-propanol)

Alcohols can be prepared by various methods, but there are only two with which we shall be concerned: the replacement of halogen by OH, and the hydrolysis of esters. The general equation

$$RX + KOH \longrightarrow ROH + KX$$

where $X = Cl$, Br, or I, illustrates the first method. It tells us that halogens attached to carbons can be replaced by refluxing them with solutions of KOH. Thus, by boiling isopropyl bromide with KOH, isopropyl alcohol can be made, and tertiary butyl alcohol can be prepared by boiling tertiary butyl bromide with KOH.

One of the most important properties of esters is that they can be hydrolyzed by boiling with alkali, the products of the reaction being a salt of the organic acid and an alcohol.

$$RCOOR' + KOH \longrightarrow RCOOK + R'—OH$$

We are interested in this reaction because fats and oils are esters and when hydrolyzed with NaOH produce soap and glycerin.

PROPERTIES OF ALCOHOLS

The textile chemist is interested in four properties of alcohols, namely, acylation, oxidation, formation of alcoholates, and reactions with acids.

Acylation is a reaction by which a hydrogen of an alcohol or amine is replaced by an acyl group, $R—CO—$ (acetyl = $CH_3—CO—$, propionyl = $C_2H_5—CO—$, benzoyl = $C_6H_5—CO—$). If the hydrogen of an alcohol, $R'OH$, is replaced by an acyl group, $R—CO—$, the product will be $R'O—CO—R$ (or $RCOOR'$), which is an ester. An acylating agent, of course, must have the acyl group in it, and there are two important classes of acylating agents, acid chlorides, RCOCl, and acid anhydrides, $(R{-}CO)_2O$. When alcohols are treated with either of these reagents they are acylated and the product is an ester.

$$R'OH + RCOCl \longrightarrow RCOOR' + HCl$$

$$R'OH + (RCO)_2O \longrightarrow RCOOR' + RCOOH$$

For example, if ethyl alcohol is treated with acetyl chloride, a vigorous reaction takes place, forming the ethyl ester of acetic acid, ethyl acetate.

$$C_2H_5OH + CH_3COCl \longrightarrow CH_3COOC_2H_5 + HCl$$

Acid anhydrides are more easily controlled acylating agents, so if we wish to acetylate ethyl alcohol we may use acetic anhydride,

$$C_2H_5OH + (CH_3CO)_2O \longrightarrow CH_3COOC_2H_5 + CH_3COOH$$

This is the reaction used in the manufacture of cellulose acetate rayon, which is discussed in detail in Chapter 8.

Alcohols can be oxidized by the ordinary oxidizing agents such as $KMnO_4$ or dichromate and acid, primary alcohols yielding aldehydes and acids, and secondary alcohols yielding ketones, as shown in the following equations.

$$\underset{\text{(propyl alcohol)}}{CH_3{-}CH_2{-}CH_2OH} \xrightarrow{[O]} \underset{\text{(propiomaldehyde)}}{CH_3{-}CH_2{-}CHO}$$

$$\underset{\text{(propiomaldehyde)}}{CH_3{-}CH_2{-}CHO} \xrightarrow{[O]} \underset{\text{(propionic acid)}}{CH_3{-}CH_2{-}COOH}$$

$$\underset{\text{(secondary propyl alcohol)}}{CH_3{-}CHOH{-}CH_3} \xrightarrow{[O]} \underset{\text{(dimethyl ketone)}}{CH_3{-}CO{-}CH_3}$$

Primary and secondary alcohol groups are found in cellulose and play an important part in the bleaching of cotton, because bleaching is an oxidation reaction (page 176).

The word alcoholate means salt of an alcohol, that is, an alcohol in which the OH hydrogen has been replaced by a metal. Such compounds can be made by adding metallic sodium or potassium to anhydrous alcohols,

$$\underset{\text{(ethyl alcohol)}}{2C_2H_5OH} + 2Na \longrightarrow \underset{\text{(sodium ethylate)}}{2C_2H_5ONa} + H_2$$

This shows that alcohol is an acid, but it is an extremely weak acid, weaker than water, and therefore if water is added to sodium ethylate it will liberate the weaker acid. This is an example of the old rule that a weak acid can be liberated from its salts by the action of a stronger acid; e.g., when H_2SO_4 is added to sodium acetate, acetic acid is formed. Another way to say the same thing is that sodium ethylate is completely decomposed or hydrolyzed by water. This means that the salt cannot be produced by treating alcohol with a solution of NaOH because of the water present in the solution. Perhaps when very strong solutions of NaOH are used, some alcoholate may be present in equilibrium with alcohol and NaOH.

$$\mathrm{ROH} + \mathrm{NaOH} \rightleftarrows \mathrm{RONa} + \mathrm{HOH}$$

Such an assumption will be made when we come to the study of mercerized cotton (page 161).

The reaction between alcohols and organic acids, to form esters, is of considerable interest because it forms the basis for the manufacture of some of the condensation polymer resins which can be plasticized. The most general reaction is

$$\mathrm{RCOOH} + \mathrm{R'OH} \rightleftarrows \mathrm{RCOOR'} + \mathrm{HOH}$$

Note that this is the same product that can be obtained by the acylation of an alcohol with either an acid chloride or acid anhydride. Since esters can be hydrolyzed back to acids and alcohols, the above reaction is reversible, but, when carried out in the presence of reagents that will remove the water as it is formed, the reaction can be forced to the right, and good yields of ester can be obtained.

Now extend the possibilities a little by using an acid with two carboxyl groups, such as $HOOC—CH_2—COOH$. This acid may react with either one or two molecules of an alcohol to form either $HOOC—CH_2—COOR'$ or $R'OOC—CH_2—COOR'$. Suppose we extend the possibilities still further by using a dicarboxylic acid (two COOH groups) and a dihydric alcohol (two OH groups).

$$\mathrm{HOOC{-}CH_2{-}CO}\boxed{\mathrm{OH + H}}\mathrm{OCH_2{-}CH_2OH} \longrightarrow$$

$$\mathrm{HOOC{-}CH_2{-}COOCH_2{-}CH_2OH} + \mathrm{HOH}$$

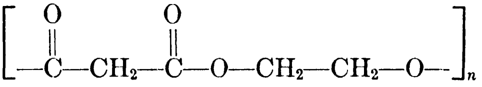
This is a condensation reaction in which the carbon chains have been lengthened and a molecule of water eliminated. But note that the product still contains some functional groups. At the left end of the formula is a COOH group which can react with more alcohol, and at the right end is an alcohol group which can react with more acid. Suppose both these reactions take place.

$$HOCH_2{-}CH_2O\boxed{H+HO}OC{-}CH_2COOCH_2{-}CH_2O\boxed{H+HO}OC{-}CH_2{-}COOH$$

The product will have five more carbons in the chain and will have the formula

$$HOCH_2{-}CH_2O[OC{-}CH_2{-}COOCH_2{-}CH_2O]OC{-}CH_2{-}COOH$$

This compound still has the same two functional groups in it and therefore may react with more acid and alcohol. By use of proper conditions and condensing agents, compounds containing very long chains can be made. These are called condensation polymers. They will have a certain pattern of repeated units or fragments. In the present example of condensation polymerization, each fragment should contain five carbons (two from the alcohol and three from the acid) and two oxygens, and this unit, which will repeat itself time after time along the chain, will be the one enclosed in brackets in the above formula. Thus the formula for the high-molecular-weight polymer can be written as follows:



$$\left[{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}CH_2{-}O{-} \right]_n$$

where n is a large number. This does not show the end groups, alcohol and acid, but they constitute such a small percentage of the total that they have nothing to do with the physical properties of the resin or the plastic which can be made from it.

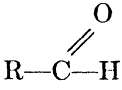
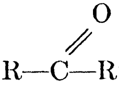
Nylon is made by such a condensation polymerization reaction, using amino compounds (NH_2 compounds) instead of alcohols (see page 312).

In the preceding short discussion of the reaction between alcohols and organic acids we have talked about alcohols with two OH groups, dihydric alcohols. Alcohols may also contain more than two OH groups, and these, as a class, are known as the polyhydric alcohols. Glycerin is the simplest trihydric alcohol, $CH_2OH{-}CHOH{-}CH_2OH$. It is found in all animal and vegetable fats and oils combined with fatty acids, and it can be separated from them by alkaline hydrolysis (saponification). This is the reaction used in soapmaking. One important use for glycerin is in the manufacture of explosives, and in the textile industry it is sometimes used as a softening agent in finishing cotton goods.

Other examples of polyhydric alcohols are the simple sugars, such as glucose, $CH_2OH—CHOH—CHOH—CHOH—CHOH—CHO$, which for the most part exists in a ring form containing five OH groups; cellulose is a high polymer consisting of repeated anhydro-glucose units having three OH groups. (See page 125.) Thus the chemistry of cotton is closely associated with the chemistry of the polyhydric alcohols.

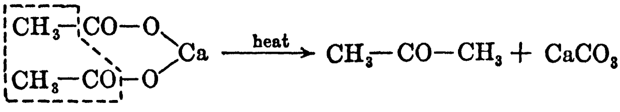
Aldehydes and Ketones

These two families of organic compounds have similar structures and similar properties, and they are prepared by similar methods; therefore we shall discuss them in the same section.

The general formula for aldehydes is  $R—\overset{\overset{O}{/\!/}}{C}—H$, or $R—CHO$, and for ketones the formula is  $R—\overset{\overset{O}{/\!/}}{C}—R'$, or $R—CO—R'$. The similarity in structures is easily seen. Both aldehydes and ketones have the $R—CO$ group, and the difference between them lies in what is attached to this group—an H in aldehydes and an R in ketones. This does not look like much of a difference, and yet some of the most important distinguishing properties of these compounds depend on this small difference.

We shall discuss three general methods for preparing aldehydes and ketones: (*a*) by the pyrolysis of salts and acids, (*b*) by the oxidation of alcohols by oxidizing agents, and (*c*) by the catalytic oxidation of alcohols.

The word pyrolysis means decomposition by heat, and thus if solid calcium acetate is decomposed when it is heated to a high temperature we can say it is being pyrolyzed. As a result of such a treatment, acetone, the simplest ketone, is formed. Acetone is a very important organic solvent and reagent, and it has been manufactured in large amounts by this method. To make this a general method, merely change the CH_3 group to R.



$$(CH_3—CO—O)_2Ca \xrightarrow{\text{heat}} CH_3—CO—CH_3 + CaCO_3$$

We have already learned that alcohols can be oxidized, primary alcohols yielding aldehydes and secondary alcohols yielding ketones, as shown below.

$$R\text{—}CH_2OH \xrightarrow{\text{oxidize}} R\text{—}CHO + HOH$$

$$R\text{—}CHOH\text{—}R \xrightarrow{\text{oxidize}} R\text{—}CO\text{—}R + HOH$$

A good oxidizing agent for such reactions is a mixture of potassium dichromate and sulfuric acid. This method gives good yields of ketones but is not satisfactory for making aldehydes, because they are further oxidized to acids and it is difficult to separate them from the reaction mixture before this happens.

The catalytic oxidation of alcohols is a high-temperature vapor-phase reaction in which vapors of alcohol are passed through hot copper or brass tubes in the presence of air. Primary alcohols are oxidized to aldehydes, and secondary alcohols to ketones. This method is used industrially with quite satisfactory results.

The most important method for the commercial manufacture of acetaldehyde, $CH_3\text{—}CHO$, consists of passing acetylene gas, C_2H_2, through a solution of sulfuric acid containing mercuric salts. The salts catalyze the addition of water to acetylene, forming the aldehyde.

$$HC{\equiv}CH + HOH \longrightarrow CH_3\text{—}CHO$$

As far as individual compounds are concerned, only three of them are of any popular interest: formaldehyde, HCHO, the well-known fumigant; acetaldehyde, $CH_3\text{—}CHO$; and acetone, $CH_3\text{—}CO\text{—}CH_3$. However, the functional groups of aldehydes and ketones, no matter where they are found, are of great interest to chemists. This is especially true in the field of cellulose chemistry, where some of the most important problems are connected with the chemistry of aldehydes and ketones.

We are interested in only three of the many chemical properties of the —CHO group, which is the functional group of all aldehydes. These are its ease of oxidation, the addition of bisulfites, and the reaction with amines. When we say that a compound can be easily oxidized, it is the same as saying that the substance is a reducing agent. Therefore we know that aldehydes are reducing agents.

Evidence of this reducing property is the fact that aldehydes will reduce Fehling's solution and ammoniacal silver oxide.

Fehling's solution is used as a test for many reducing substances and therefore can be used as a test for the aldehyde group. This is important in textile chemistry because these groups are formed when cotton and linen are overbleached. Fehling's solution is a dark blue solution made by mixing two solutions, (*a*) a solution of copper sulfate and (*b*) a strongly alkaline solution of sodium potassium tartrate. When these two solutions are mixed cupric hydroxide is formed, but it is kept in solution by forming a complex compound with the tartrate. For all practical purposes Fehling's solution may be considered an alkaline solution of cupric oxide, CuO. If a good reducing agent is added to hot Fehling's solution, the cupric oxide will be reduced to cuprous oxide, Cu_2O (the expected change from the *ic* form to the *ous* form). The visible evidence of this reduction is the precipitation of Cu_2O, a brownish red solid. Thus, when a compound containing aldehyde groups is added to hot Fehling's solution, a brownish red precipitate will be formed, and the amount of the precipitate will be a measure of the amount of aldehyde group present in the substance. This is a quite sensitive test. For example, if a slightly overbleached cotton is put into boiling Fehling's solution, the cloth will be stained a brownish red. That is, cuprous oxide will have been formed, but not enough to precipitate to the bottom of a beaker. The amount of it is too small for that, and yet at the surface of the cloth, where the aldehyde groups have been formed by a little too much bleaching (oxidation), the reaction will take place; cuprous oxide will be formed, and it will adhere to the cloth, causing a reddish brown stain. There is a quantitative method for determining the exact amount of cuprous oxide deposited on the cotton. This determination, which tells us the copper number of the cotton, will be discussed in Chapter 7. The general equation for the Fehling's solution test is

$$XCHO + 2CuO \longrightarrow Cu_2O + XCOOH$$

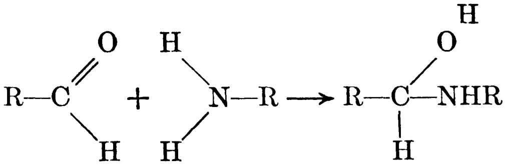
where X represents perhaps an unknown part of a complex compound. The cupric oxide is reduced to cuprous oxide, and the aldehyde group is oxidized to the carboxyl group.

Products formed by the addition of bisulfites and hyposulfites to an aldehyde are important in the textile industry. When zinc dust is added to a solution of sodium bisulfite ($NaHSO_3$) and SO_2 is passed in (forming sulfurous acid, H_2SO_3), the product is sodium hyposulfite, which will crystallize with two molecules of water of crystallization

$$Zn + 2NaHSO_3 + H_2SO_3 \longrightarrow \underset{\substack{\text{(sodium}\\\text{hyposulfite)}\\\text{(sodium}\\\text{hydrosulfite)}}}{Na_2S_2O_4} + ZnSO_3 + 2H_2O$$

Sodium hyposulfite will hydrolyze to a certain extent to a mixture of $NaHSO_3$ and $NaHSO_2$, and so when commercial preparations of sodium hyposulfite are used we may consider the reagent to be a mixture of $NaHSO_3$ and $NaHSO_2$. The latter is sometimes called sodium sulfoxylate. For use in the textile industry, sodium hyposulfite is added to a solution of formaldehyde to form a mixture of two addition products, sodium bisulfite formaldehyde and sodium sulfoxylate formaldehyde. These products are marketed under such names as Hyraldite, Sulfoxite, Rongalite, Formosul, Hydrosulfite, and Blankite. These compounds are crystalline solids that are quite stable, but when exposed to steam they decompose and $NaHSO_2$ and $NaHSO_3$ are liberated in an active form. For this reason the formaldehyde addition compounds are good reducing agents, which are used as discharging agents in calico printing and reducing agents for indigo dyeing.

Aldehydes not only will add bisulfites but they will add amines, e.g.,



This is a general equation for such an addition, but in textile technology formaldehyde is the only aldehyde that is used. Many finishes and protective agents have been produced by the action of formaldehyde with some simple and complex amino compounds. Two of these addition compounds are being used for various specific purposes. They are the urea formaldehydes and the melamine formaldehydes, made by combining formaldehyde with urea and melamine, respectively. (See page 203.) These addition compounds can be polymerized on cotton and wool to produce new finishes on the cotton and to protect wool against laundering shrinkage. Both these uses will be discussed in later chapters.

Acids

The organic carboxylic acids have the general formula RCOOH, in which the functional group is the carboxyl group, —COOH. The hydrogen of this group is the acid hydrogen of the compound, the one that is replaceable by a metal to form a salt, or by an alkyl group to form an ester. The monobasic acids (having only one carboxyl group) make up a family known as the fatty acids, so called because many of them are found in animal and vegetable oils and fats combined with glycerin. They are of interest to the textile chemist for this reason, and also because individual members of the family, and their derivatives, are used for special purposes in the textile industry.

TABLE 4

The Fatty Acids

Name	Formula	Melting Point, °C	Boiling Point, °C	Specific Gravity
Formic	HCOOH	8.4	100.5	1.22
Acetic	CH_3COOH	16.7	118.1	1.05
Propionic	C_2H_5COOH	−22.0	141.1	0.99
Butyric	C_3H_7COOH	−7.9	163.5	0.96
Valeric	C_4H_9COOH	−59.0	187.0	0.94
Caproic	$C_5H_{11}COOH$	−5.2	202.0	0.93
Caprylic	$C_7H_{15}COOH$	16.3	237.0	0.91
Capric	$C_9H_{19}COOH$	31.0	268.0	0.90
Lauric	$C_{11}H_{23}COOH$	43.8		0.88
Myristic	$C_{13}H_{27}COOH$	54.0		0.86
Palmitic	$C_{15}H_{31}COOH$	67.4		0.85
Stearic	$C_{17}H_{35}COOH$	69.2		0.85
Oleic	$C_{17}H_{33}COOH$	14.0		0.89
Linoleic	$C_{17}H_{31}COOH$	−18.0		0.92
Linolenic	$C_{17}H_{29}COOH$			

The names applied to the fatty acids are old ones that originally had some connection with the natural sources of the acids. The most important of them are listed in Table 4.

The carboxylic acids can be prepared (1) by the oxidation of alcohols and aldehydes, and (2) by the hydrolysis of nitriles, amides, and esters. The first method has already been discussed. Hydrolysis methods are usually carried out by boiling in acid medium, the organic acid and an inorganic salt or alcohol being formed. Examples are:

$$\underset{\text{(nitrile)}}{RCN} + 2HOH \xrightarrow{HCl} RCOOH + NH_4Cl$$

$$\underset{\text{(amide)}}{RCONH_2} + HOH \xrightarrow{HCl} RCOOH + NH_4Cl$$

$$\underset{\text{(ester)}}{RCOOR'} + HOH \xrightarrow{HCl} RCOOH + R'OH$$

The fatty acids can be liberated from their salts by treating with a strong acid

$$RCOONa + H_2SO_4 \longrightarrow RCOOH + NaHSO_4$$

This equation illustrates an important general rule, that a weak acid can be liberated from its salts by the action of a strong acid. (Likewise, a weak base can be liberated from its salts by the action of a strong base.) In textile chemistry one of the best examples of this is the reaction of soap with mineral acid. Soap is a salt of a mixture of very weak acids; when it is treated with a strong acid, these weak organic soap acids (fatty acids) are liberated.

The salts and esters of acids are named by changing the syllable "ic" in the acid to "ate"; e.g., CH_3COONa is sodium acetate, $(CH_3COO)_2Ba$ is barium acetate, $C_{17}H_{35}COOK$ is potassium stearate, $CH_3COOC_2H_5$ is ethyl acetate, and $C_3H_7COOCH_3$ is methyl butyrate.

PROPERTIES AND DERIVATIVES OF ACIDS

The functional group of fatty acids is the carboxyl group, —COOH, and to this group they owe their action as acids. When an acid is treated with a base, the product is a salt in which a metal has replaced the acid hydrogen of the acid.

$$RCOOH + NaOH \longrightarrow RCOONa + HOH$$

The salts of the lower fatty acids are crystalline solids, but the salts of the higher-molecular-weight acids are not crystalline. For example, sodium acetate (CH_3COONa) is a white crystalline solid, soluble in water to form a true solution. On the other hand, sodium stearate ($C_{17}H_{35}COONa$) is not a crystalline but an amorphous semi-waxy solid like soap; in fact, its formula may be used to represent a soap. Sodium stearate is not very soluble in water, and its solutions do not have the properties of true salt solutions but of colloidal solutions.

Salts of organic acids react with other salts, just as inorganic salts do, to form another salt with a lower solubility. This is illustrated by the action of hard water on soap solution. Hardness in water is caused by the presence of calcium and magnesium ions, which will react with soap to form insoluble calcium or magnesium soaps. If we let sodium palmitate represent the soap and $CaSO_4$ represent hard water, the equation will be

$$2C_{15}H_{31}COONa + CaSO_4 \longrightarrow (C_{15}H_{31}COO)_2Ca + Na_2SO_4$$

Calcium palmitate is insoluble in water and is observed as a scum on the surface of the water.

Salts of high-molecular-weight fatty acids (such as soap) are decomposed by high temperature. They first soften, then begin to darken, and become black (carbon); finally the black disappears, leaving a white residue of carbonate.

$$C_{15}H_{31}COONa + \text{heat and air} \longrightarrow Na_2CO_3 + CO_2 + H_2O$$

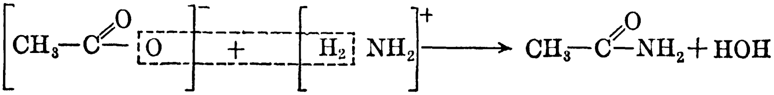
When the acid hydrogen of fatty acids is replaced by an alkyl group (or similar carbon and hydrogen groups), the product is an ester. All animal and vegetable fats and oils contain such compounds, mostly the glyceryl esters of a mixture of high-molecular-weight acids. These are combinations of glycerin and fatty acid. Waxes are esters of these same acids combined with much higher-molecular-weight alcohols. For example, spermacetti wax contains cetyl palmitate, $C_{15}H_{31}COOC_{16}H_{33}$, a combination of palmitic acid with cetyl alcohol. Carnauba wax and beeswax contain large amounts of myricyl palmitate, $C_{15}H_{31}COOC_{31}H_{63}$. These natural waxes are used in dressings for textile materials, as softening agents, and for waterproofing cottons.

The most important property of esters is hydrolysis, which is represented by

$$RCCOOR' + HOH \rightleftarrows RCOOH + R'OH$$

However, this does not mean that the ester will react with water. Such hydrolyses must be carried out in either acid or alkaline medium and usually with long boiling. If the medium is acid, the product is a mixture of fatty acid and alcohol. If the medium is alkaline, the process is usually called saponification, and the product is a mixture of the salt of the acid and alcohol. This alkaline hydrolysis, or saponification, is the important reaction in soap manufacture, in which a fat (a glyceryl ester) is saponified to yield soap and glycerin.

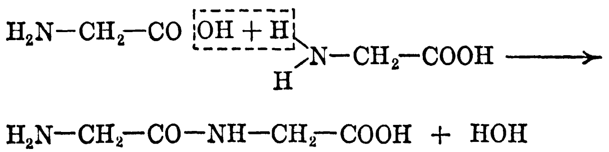
The amides are among the most important derivatives of acids. An amide has the general formula $R—CO—NH_2$ and, therefore, may be considered a fatty acid in which the $—OH$ group has been replaced by the amino group $—NH_2$. Amides can be made by heating ammonium salts of organic acids. An ammonium salt is one in which the acid hydrogen has been replaced by NH_4; e.g., ammonium acetate is CH_3COONH_4. These ammonium salts are true salts, which means that the solid salts are composed of positive and negative ions arranged in some well-oriented structure. When such salts are heated to a high temperature, the ions condense with each other and eliminate a molecule of water, and the result is an amide, as shown by



$$\left[CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-O\right]^- + \left[H_2\,NH_2\right]^+ \longrightarrow CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-NH_2 + HOH$$

In many amides the two hydrogens attached to the nitrogen may be replaced by alkyl or other organic radicals, so that this reaction is a very general one. That is, a real ammonium salt of an organic acid or anything like an ammonium salt can be pyrolyzed to form something like an amide. The net result of this amounts to a condensation between organic acids and ammonia derivatives to form amides.

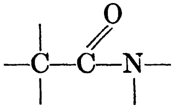
Suppose that we have the proper conditions for the condensation of two molecules of glycine, $H_2N—CH_2—COOH$, an amino acid. The reaction would be



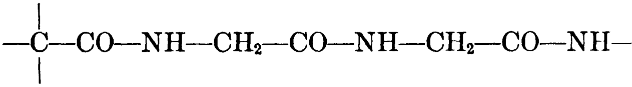
$$H_2N-CH_2-CO\,OH + \genfrac{}{}{0pt}{}{H}{H}\!\!>N-CH_2-COOH \longrightarrow$$

$$H_2N-CH_2-CO-NH-CH_2-COOH + HOH$$

Part of the skeleton structure of this condensation product is very important. It is the fragment that is known as the peptide link-



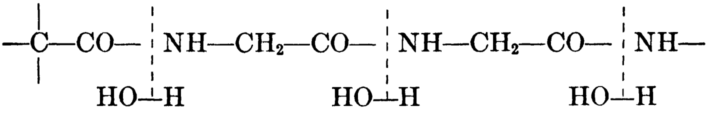
age and is found in all protein substances (wool and silk). Since this compound has both an —NH$_2$ group and a —COOH group, it can condense with other amino acids, and this could continue until long-chain molecules would be formed in which the peptide linkage would be repeated.



$$-\overset{|}{\underset{|}{C}}-CO-NH-CH_2-CO-NH-CH_2-CO-NH-$$

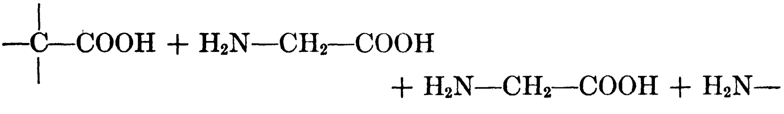
The H's in this formula may be replaced by a variety of other groups, so that a natural protein has a very complex structure. Some synthetic polypeptides have properties resembling those of the natural proteins, but the natural proteins are very much more complex.

Since wool and silk are animal fibers, and therefore protein fibers, we shall be very much concerned with the chemistry of the polypeptides and the peptide linkage. The most important property of this linkage is that it can be split by alkaline hydrolysis.



$$-\overset{|}{\underset{|}{C}}-CO-\,\underset{HO-H}{\vdots}\,NH-CH_2-CO-\,\underset{HO-H}{\vdots}\,NH-CH_2-CO-\,\underset{HO-H}{\vdots}\,NH-$$

yielding



$$-\overset{|}{\underset{|}{C}}-COOH + H_2N-CH_2-COOH + H_2N-CH_2-COOH + H_2N-$$

Note that the products of the hydrolysis of a polypeptide are amino acids, but, since the hydrolysis is carried out in alkaline medium (NaOH), the acids will exist as their sodium salts, and these salts will be soluble in water. The fact that wool and silk are so sensitive to the action of alkalies and so easily damaged by them is due to this reaction. When natural proteins are hydrolyzed the reaction is perfectly analogous but a complex mixture of salts of amino acids is obtained. In all these amino acids the NH$_2$ groups are attached to the alpha carbon atom, that is, the carbon adjacent to the COOH group of the acid. This means that the hydrolysis of a true polypeptide will yield alpha amino acids.

Students of textile chemistry are interested in only four proteins, the keratin of wool, the fibroin of silk, the casein of milk, and the zein of corn. Table 5 lists the names, formulas, and percentage of the amino acids that make up the complex structures of these proteins. The figures have been taken from *The Amino Acid Composition of Proteins and Foods* by Block and Bolling, published by Charles C. Thomas, 1945. These figures are the result of a critical summarizing of the best work done in this field, and in order to have them strictly comparable they have all been calculated to a 16% nitrogen content. The acids are arranged alphabetically rather than according to their chemical structural classification.

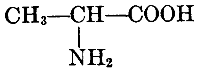
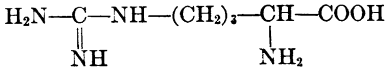
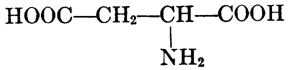
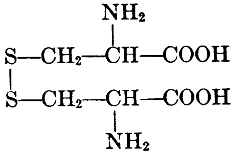
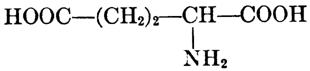
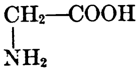
A reaction similar to the formation of a peptide linkage is used in the manufacture of nylon. Nylon is the same kind of long-chain compound except that in place of the one $—CH_2—$ group in the above formula there are four and six $—CH_2—$ groups between the —NH— and —CO— groups. This is not a true peptide linkage and is not nearly as sensitive to the action of alkalies.

Many compounds important in textile chemistry may be considered as derivatives of fatty acids in which certain hydrogens of the alkyl part of the acid have been substituted by other groups. The most important of these are the $—NH_2$ and the —OH groups which are found attached to the alpha carbon of the acid. Lactic acid (alpha hydroxy propionic acid) is an important hydroxy acid, and the amino acids (as shown in Table 5) are the products of the hydrolysis of proteins.

The introduction of a second carboxyl group into an acid, to make it a dibasic acid with two acid hydrogens, has a profound effect on the physical properties of the acid. It raises the melting point enormously. Thus acetic acid, with two carbons, melts at 16° C, whereas oxalic acid, the dicarboxylic acid with two carbons (HOOC—COOH), melts at 189° C. It also affects the physical form, as shown by the fact that all the dicarboxylic acids are crystalline solids, whereas the solid fatty acids are not crystalline. As far as chemical properties are concerned, the dibasic acids have the same properties and derivatives, salts, esters, amides, etc., as the monocarboxylic acids.

TABLE 5

Amino Acids from Proteins

		Percentages of Amino Acids in Four Protein Substances (Calculated to a 16% Nitrogen Content)			
Amino Acid	Formula	Wool	Silk Fibroin	Casein	Zein
Alanine	 $CH_3\text{—}\underset{NH_2}{\underset{\vert}{CH}}\text{—}COOH$	4.0	22.2	5.6	9.9
Arginine	 $H_2N\text{—}\underset{NH}{\underset{\Vert}{C}}\text{—}NH\text{—}(CH_2)_3\text{—}\underset{NH_2}{\underset{\vert}{CH}}\text{—}COOH$	10.0	0.9	4.1	1.6
Aspartic acid	 $HOOC\text{—}CH_2\text{—}\underset{NH_2}{\underset{\vert}{CH}}\text{—}COOH$	7.3	....	6.3	3.4
Cystine	 $\begin{array}{l} S\text{—}CH_2\text{—}\overset{NH_2}{\overset{\vert}{CH}}\text{—}COOH \\ \vert \\ S\text{—}CH_2\text{—}\underset{NH_2}{\underset{\vert}{CH}}\text{—}COOH \end{array}$	11.1	....	0.4	0.8
Glutamic	 $HOOC\text{—}(CH_2)_2\text{—}\underset{NH_2}{\underset{\vert}{CH}}\text{—}COOH$	15.3	....	22.8	35.6
Glycine	 $\underset{NH_2}{\underset{\vert}{CH_2}}\text{—}COOH$	7.0	36.8	0.5	0.0

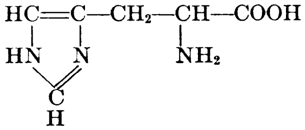
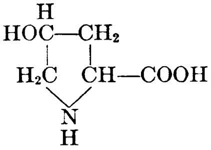
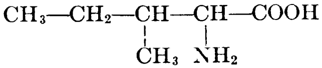
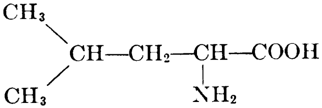
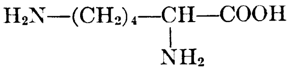
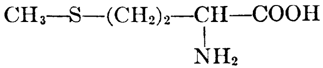
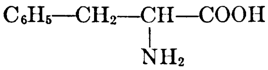
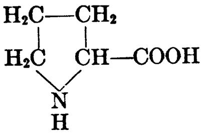
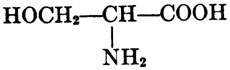
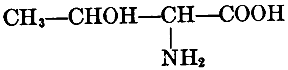
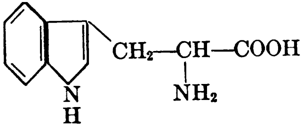
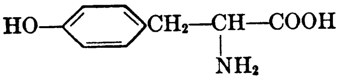
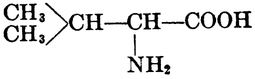
Histidine		0.7	0.06	2.5	0.9
Hydroxyproline		....	....	2.0	0.0
Isoleucine	 $CH_3—CH_2—CH(CH_3)—CH(NH_2)—COOH$	...	....	....	4.3
Leucine		11.0	0.8	18.6	23.7
Lysine	 $H_2N—(CH_2)_4—CH(NH_2)—COOH$	3.0	0.2	6.9	0.0
Methionine	 $CH_3—S—(CH_2)_2—CH(NH_2)—COOH$	0.6	....	3.5	2.4
Phenylalanine	 $C_6H_5—CH_2—CH(NH_2)—COOH$	3.9	....	5.2	6.4

TABLE 5—*Continued*

Amino Acid	Formula	Percentages of Amino Acids in Four Protein Substances (Calculated to a 16% Nitrogen Content)			
		Wool	Silk Fibroin	Casein	Zein
Proline		9.3	1.0	8.2	9.0–12.0
Serine	 $HOCH_2-\underset{NH_2}{\underset{\vert}{CH}}-COOH$	....	11.4	6.0–7.0	....
Threonine	 $CH_3-CHOH-\underset{NH_2}{\underset{\vert}{CH}}-COOH$	....	1.3	3.9	2.4
Tryptophane		1.5	....	1.8	0.1
Tyrosine		5.1	11.1	6.4	5.0
Valine	 $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH-\underset{NH_2}{\underset{\vert}{CH}}-COOH$	4.0–5.0	2.7	7.0	2.4

Amines

Amines are nitrogenous organic compounds containing —NH_2, or alkylated —NH_2 groups, which can be subdivided into three classes: primary amines, RNH_2; secondary amines, R_2NH; and tertiary amines, R_3N. These general formulas indicate that they are aliphatic compounds, but some of the most important amines are aromatic, derived from the mother substance aniline, $C_6H_5NH_2$. The so-called aniline dyes are derived from aniline.

Aliphatic amines may be prepared:

(1) By the alkaline hydrolysis of mono or dialkylated amides

$$RCO{-}NHR' + NaOH \longrightarrow RCOONa + R'NH_2$$

$$RCO{-}NR_2' + NaOH \longrightarrow RCOONa + R_2'NH$$

Owing to this reaction many complex nitrogenous organic compounds will yield some amines when hydrolyzed in alkaline medium.

(2) By the alkaline hydrolysis of isocyanates

$$R{-}N{=}C{=}O + 2NaOH \longrightarrow RNH_2 + Na_2CO_3$$

(3) By the Hofmann reaction, which consists of heating an amide with NaOH and Br_2 (sodium hypobromite). Note that one carbon atom is lost during this reaction, so that the resulting amine has one carbon less than the original amide.

$$RCONH_2 + 4NaOH + Br_2 \longrightarrow RNH_2 + Na_2CO_3 + 2NaBr + HOH$$

(4) By the reduction of nitriles (organic cyanides). This may be accomplished by dissolving the nitrile in absolute alcohol and adding metallic sodium in small portions.

$$RCN + 4Na + 4C_2H_5OH \longrightarrow RCH_2{-}NH_2 + 4C_2H_5ONa$$

Aromatic primary amines in which the —NH_2 group is attached to an aromatic ring are prepared by the acid reduction of a nitro group, —NO_2, with zinc and hydrochloric acid.

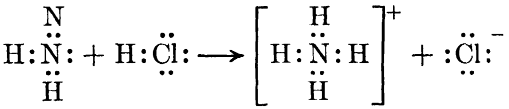
$$C_6H_5NO_2 + 3Zn + 6HCl \longrightarrow C_6H_5NH_2 + 3ZnCl_2 + 2HOH$$

Alkaline reducing agents cannot be used in this reaction.

The amines may be considered derivatives of ammonia, NH_3, in which one or more of the hydrogens have been replaced by alkyl groups or aromatic rings. Because of this relationship the amines should behave like ammonia. The outstanding property of ammonia is that it is a base and will react with an acid. When an acid reacts with a base the product is a salt in which there is a positive ion in place of the acid hydrogen of the acid. Water may or may not be another product. The most fundamental concept of a base is that it is a compound with unshared electrons which can accept a proton (a hydrogen atom without any electrons, a hydrogen ion). Conversely, an acid is a substance which can donate a proton, or hydrogen ion. We know that ammonia will react with hydrochloric acid to form ammonium chloride,

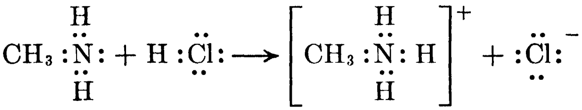
$$NH_3 + HCl \longrightarrow NH_4Cl$$

and if we look at the electronic structures we find that NH_3 has an unshared pair of electrons on the nitrogen, to which a proton can attach itself to make NH_4^+ ion, leaving the chlorine atom as a chloride ion



$$\mathrm{H}:\overset{\mathrm{N}}{\underset{\mathrm{H}}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}}}}: + \mathrm{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}: \longrightarrow \left[\ \mathrm{H}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}}}}:\mathrm{H}\ \right]^{+} + :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:^{-}$$

Thus we see that the basicity of ammonia is due to the unshared pair of electrons that will accept a proton. We find this same situation in the amines, and therefore they are basic compounds like ammonia and will form salts with acids.



$$\mathrm{CH_3}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}}}}: + \mathrm{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}: \longrightarrow \left[\ \mathrm{CH_3}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}}}}:\mathrm{H}\ \right]^{+} + :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:^{-}$$

(methylamine hydrochloride)

Sometimes the formula is written differently; e.g., aniline reacts with hydrochloric acid to form aniline hydrochloride, $C_6H_5NH_2$—HCl.

These salts are salts of weak bases, and therefore the free amine (base) can be liberated from its salts by the action of a strong base such as NaOH

$$C_6H_5NH_2\text{—}HCl + NaOH \longrightarrow C_6H_5NH_2 + NaCl + HOH$$

The reaction between amines and chlorine or hypochlorites is of interest to us because it tells us why wool and silk cannot be bleached with ordinary bleach liquor (calcium hypochlorite), and also it explains the first stages of the process of chlorination of wool (page 278). If a primary amine is treated with chlorine gas, the amino group is chlorinated and the two hydrogens are replaced by chlorines to form dichloramines,

$$RNH_2 + 2Cl_2 \longrightarrow RNCl_2 + 2HCl$$

This same thing can be accomplished by the use of hypochlorites (bleach liquor).

$$RNH_2 + Ca(OCl)_2 \longrightarrow RNCl_2 + Ca(OH)_2$$

It can be seen that the bleaching of wool with bleach liquor would not be satisfactory because wool contains amino groups which would be attacked as well as the colored material that is to be destroyed. Another objection to the use of hypochlorites in wool bleaching is that the chloroamines are oxidizing agents which could oxidize the wool, destroy its valuable properties, and decrease its tensile strength. Bleach liquor itself is an oxidizing agent, so that, if wool were to be bleached in this way, it would be subjected to the oxidizing action of not only hypochlorite but also the chloroamines formed by the action of hypochlorite on amino groups. We shall discuss in a later chapter (page 278) the use of hypochlorites for making chlorinated wool, where it is desirable to have the free edges of the scales on wool fibers eroded, so that the wool will not shrink when wet.

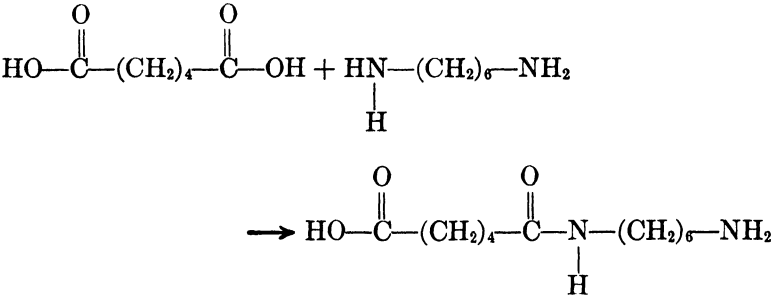
When primary amines are heated with carboxylic acids, water is eliminated and the product may be considered a condensation product like the ones produced from acids and alcohols (page 34).

$$R{-}COOH + H_2N{-}R \xrightarrow{\text{heat}} RCO{-}NHR + HOH$$

Since the amine is a base, the first product of this reaction is a salt, $R{-}COONH_3R$. When ammonium salts are heated (pyrolyzed), a molecule of water is eliminated and an amide is formed. Likewise the pyrolysis of the above amine salt would eliminate water and form an amide, in this case an alkyl amide. This is a very important reaction in the manufacture of high-polymer amide resins used in making nylon. This will be discussed in detail later, but a brief explanation of it at this point is desirable.

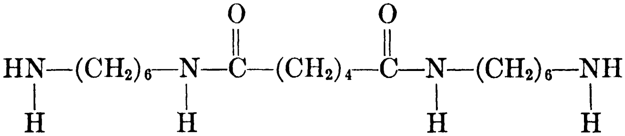
We found that some alcohols have two —OH groups (the dihydric alcohols), and now we find that some amines have two $—NH_2$

groups (the diamines). Examples of these are $H_2N-CH_2-CH_2-NH_2$, ethylenediamine, and $H_2N-(CH_2)_6-NH_2$, hexamethylenediamine. Such diamines can be condensed with dibasic acids to form long-chain polymeric amides:



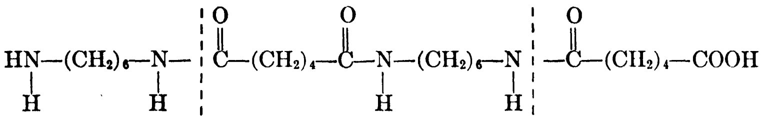
$$HO-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-OH + \underset{\underset{H}{|}}{HN}-(CH_2)_6-NH_2 \longrightarrow HO-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-(CH_2)_6-NH_2$$

Since this compound still has a COOH in it, it can condense with another molecule of the diamine. Putting this second molecule of diamine at the left, the product would be



$$\underset{\underset{H}{|}}{HN}-(CH_2)_6-\underset{\underset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-(CH_2)_6-\underset{\underset{H}{|}}{NH}$$

This could condense with more acid. Putting the acid molecule at the right, the product would be



$$\underset{\underset{H}{|}}{HN}-(CH_2)_6-\underset{\underset{H}{|}}{N}-\;\vdots\;\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-(CH_2)_6-\underset{\underset{H}{|}}{N}\;\vdots\;-\overset{\overset{O}{\|}}{C}-(CH_2)_4-COOH$$

It is seen that the fragment between the vertical dotted lines will be repeated time after time along the length of the chain. Such long-chain high-polymeric amides have been given the name nylon.

Aromatic amines are used in large amounts in the manufacture of dyes. For this purpose they are diazotized and coupled with aromatic amines, phenols, or naphthols. The diazotization reaction is carried out by dissolving an amine in an excess of acid such as HCl, and adding sodium nitrite in portions. The $NaNO_2$ will react with the excess HCl to form $HNO_2(HONO)$, which then diazotizes the amine

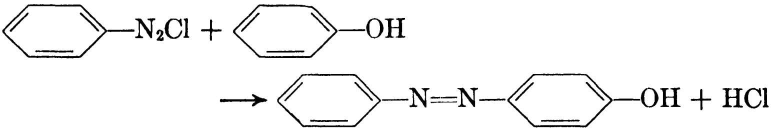
$$C_6H_5NH_2 + HCl \longrightarrow C_6H_5NH_2{\cdot}HCl$$

$$C_6H_5NH_2{\cdot}HCl + HONO \longrightarrow \underset{\text{(a diazonium chloride)}}{C_6H_5{-}N_2Cl} + 2HOH$$

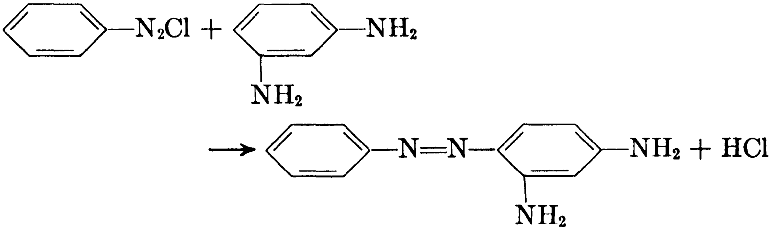
A great many amines can be diazotized, e.g., those with one NH_2 group on the ring which may also hold other substituents, those with two NH_2 groups on the ring in different positions, and those with NH_2 groups on naphthalene rings, etc. Thus a great variety of diazonium salts can be made, and each one can be coupled with any one of a large number of aromatic amines and phenols.

The coupling reaction is carried out in an alkaline or weakly acid medium, resulting in the formation of azo compounds in which two rings are joined together by the azo group, —N=N—. A few examples follow:

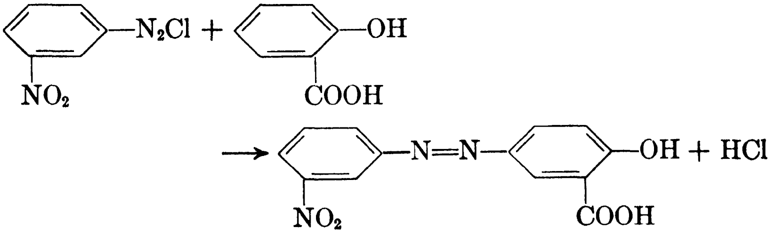
Couple diazotized aniline with phenol:



Couple diazotized aniline with *m*-phenylenediamine:



Couple diazotized *m*-nitroaniline with salicylic acid:



A large number of azo dyes are manufactured by such reaction.

3 · Soap

Water is the most important chemical substance used in the textile industry. It is the universal solvent in all wet processes connected with the manufacture of yarns and fabrics, bleaching, dyeing, laundering, and the maintenance of textile materials in the home. Soap is a close second in importance, and we shall study soap first because we shall want to know something about soap when we study the different types of water, especially hard water. One might wonder why a discussion of soap should be included in a book on textile chemistry, since soap is not a textile material, but if we consider the many ways in which it is used in the textile industry we shall conclude that no book on textile chemistry would be complete without such a study. The uses of soap will become apparent and will be discussed in detail when we study the various individual fibers.

For the present we shall discuss soap in a general way, the raw materials and methods used in its manufacture, its chemical and physical properties, the evaluation of soaps, detergency as related to soap, etc.; and later we shall study the special-purpose soaps as information about them becomes necessary. Although this chapter may seem quite abstract, remember that the substance soap is of great importance to the laundryman, the housewife, and the mill operator, no matter what fibers they may be dealing with.

A soap is a salt of a high-molecular-weight fatty acid and has a general formula RCOOMe, where Me stands for a metal. Only two metals form such salts which are soluble in water. They are sodium and potassium, and so the only soaps that have any value as cleansers are the sodium and potassium soaps. The insoluble soaps are usually called metallic soaps, and even though they have no value as cleansers they have certain other practical applications. For example, calcium soaps can be used in making adhesive plasters and axle grease; lead and manganese soaps can serve as driers in paints and varnishes; aluminum soaps are used for waterproofing cloth and concrete and for thickening lubricating oils; iron and chromium soaps are used in dyeing and cotton printing; magnesium soaps are dissolved in naphtha and used in dry cleaning. We shall be interested in soaps for cleaning and scouring, and so we shall confine our study to those soaps that are soluble in water, namely, the potassium soaps (potash soaps) often called soft soaps, and the sodium soaps, often called hard soaps.

There are two general methods by which soap can be made. Since soap is a salt of an acid it should be possible to make it from an acid and a base. If a sodium soap is to be made, a high fatty acid could be treated with sodium hydroxide.

$$\mathrm{RCOOH} + \mathrm{NaOH} \longrightarrow \mathrm{RCOONa} + \mathrm{HOH}$$

This is one of the commercial methods for manufacturing soap. But where can the fatty acids be obtained? The natural sources of the high-molecular-weight fatty acids are the animal and vegetable fats and oils, which are esters that can be hydrolyzed in alkaline medium to form soap. Even though a fat is not a simple ester we can illustrate the above statement by a general formula for the simple esters.

$$\mathrm{RCOOR'} + \mathrm{NaOH} \longrightarrow \mathrm{RCOONa} + \mathrm{R'OH}$$

The alkaline hydrolysis of an ester is given the special name "saponification," and we can say that soaps can be made by the saponification of fats; most commercial soaps are made by this method.

If, for the present, we are letting RCOOR′ represent a fat and RCOONa a soap, then differences among several commercial sodium soaps must be due to differences among the fats used to make them, that is, to differences in R. In other words, the characteristics of various sodium soaps will depend upon the characteristics of the fats or fatty acids used to make them. There is considerable variation in the characteristics of soaps. Some soaps dissolve much more easily than others; some form suds easily in cold water, whereas others require hot water; some soapsuds will break at high temperatures and others will not; some soaps become rancid and develop bad odors, but others do not. These are some of the evidences that various soaps have different qualities or characteristics, and, as stated above, these variations are due to the fats or fatty acids used in making the soaps. For this reason it is necessary that we know something about these fats and oils, their sources, and their physical and chemical properties, so that we can understand and perhaps predict the properties of soaps made from them.

FATS AND OILS

It must be clearly understood that soaps are made from animal or vegetable fats or oils, and not from mineral oils. Petroleum oils, such as lubricating oil or machine oil, cannot be used to make soap. Such oils are hydrocarbons and are not saponifiable. In other words, they are not derivatives of acids; they are not esters, and they cannot form sodium or potassium salts. So we must confine ourselves to a study of the animal and vegetable fats and oils.

The difference between a fat and an oil is purely a physical difference, one being solid at ordinary temperatures and the other a liquid. Beef tallow is a solid at room temperature and we think of it as a fat, whereas olive oil is a liquid and is thought of as an oil. But if tallow is melted it becomes a liquid like an oil, and if olive oil were cooled to a low enough temperature it would freeze and be a solid fat like tallow. Consequently the difference between a fat and an oil is merely a matter of temperature. In this chapter we shall consider all animal and vegetable fats and oils as fats, whether they are solids or liquids. That is, olive oil, cottonseed oil, corn oil, and linseed oil will be called fats, and it must be clearly understood that the word fat does not apply to any solid or liquid petroleum product, but only to the fatty substances derived from animal or vegetable sources.

Fats are esters of fatty acids, but there are two limitations on such a general statement. First, they are esters of high-molecular-weight acids, with an even number of carbon atoms; and second, the alcohol part of the esters is the glyceryl group, C_3H_5, of glycerin. Glycerin is a trihydric alcohol; that is, it is an alcohol with three OH groups, and the organic radical is the glyceryl group with a valence of 3. The formula for glycerin is

$$CH_2OH\text{—}CHOH\text{—}CH_2OH \qquad \text{or} \qquad C_3H_5(OH)_3$$

Palmitic acid is $C_{15}H_{31}COOH$, and the ethyl ester is $C_{15}H_{31}COOC_2H_5$, since both the palmitate group and the ethyl radical have a valence of 1. Ethyl palmitate is not a fat, but glyceryl palmitate is, and its formula is $(C_{15}H_{31}COO)_3C_3H_5$ because the glyceryl radical has a valence of 3. Such a compound can be named in various ways—glyceryl palmitate, the glyceryl ester of palmitic acid, the glyceride of palmitic acid, or palmitin. The last name is formed by replacing the "ic" syllable in the name of the acid by the syllable "in." This is the usual method of naming the glycerides, and we shall be talking about stearin, olein, myristin, laurin, etc., which are the glycerides of stearic, oleic, myristic, and lauric acid, respectively.

Palmitin, $(C_{15}H_{31}COO)_3C_3H_5$, is a compound that is typical of a fat, but there is no fat that has this formula, because all fats are mixtures of the glycerides of three or more high-molecular-weight fatty acids. The most important of these are stearin, palmitin, and olein, which are found in most fats. The others occur in fats in smaller amounts, but sometimes they give special characteristics to the fats.

Since fats are mixtures of glycerides, they certainly are not pure chemical compounds, and there can be no such thing as a formula for a fat. However, we can write a formula that will represent a fat. Since fats are glycerides, the formula for the glyceride of any of the fatty acids could represent a fat. For example, $(C_{17}H_{35}COO)_3C_3H_5$ is the formula for a pure chemical compound, stearin, and $(C_{15}H_{31}COO)_3C_3H_5$ is palmitin. Either one of these formulas can represent a fat, even though it would not be the real formula for any particular fat. The important thing is that, if stearin or palmitin takes part in a chemical reaction, then any fat will do the same thing, and so the formula for pure stearin may represent any fat, as far as chemical equations are concerned. We might generalize still more and use the formula $(RCOO)_3C_3H_5$ as representing a fat. The conventional meaning of R, an alkyl group, is a saturated chain of carbon atoms, but we know that many of the glycerides found in fats are unsaturated. Therefore, if a fat is represented by $(RCOO)_3C_3H_5$, it must be understood that R is either a saturated or unsaturated chain of carbons. Similarly, when we talk about the mixed fatty acids obtained from a fat, it must be understood that some of them are saturated and others are unsaturated. These things are not just of academic interest; some of the most important properties of fats, fatty acids, and soaps depend on them. These will become apparent as our study progresses.

Table 6 shows some of the fats suitable for making soap. The second column shows whether they are liquids or solids at ordinary temperatures. The third column shows the range of the iodine value for each fat. The numbers in this column are percentages of iodine that a fat will absorb. Iodine will add to ethylenic double bonds, and therefore the iodine value of a fat is a measure of the relative amount of unsaturation in the fat. Another way to think of the iodine value is that it is the number of grams of iodine that will be absorbed by 100 gm of fat. The unsaturation in a fat will be carried over into a soap made from it and will be an important factor in determining the characteristics of the soap.

TABLE 6

Physical and Chemical Constants of Some Common Fats

Fat	Solidification Point, ° C	Iodine Value, %	Titer of Mixed Fatty Acids, ° C
Beef tallow	30–38	32–47	38–47
Palm oil	31–39	51–58	36–45
Lard	22–32	46–66	34–42
Wool grease	30–40	15–30	38–40
Cottonseed oil	0–5	103–111	33–38
Peanut oil	0–3	85–98	23–29
Soybean oil	−18 to −8	124–133	21–24
Palm kernel oil	19–24	15–18	20–25
Coconut oil	19–23	8–10	20–22
Linseed oil	−27 to −18	170–185	19–21
Olive oil	−6 to +2	80–85	17–21
Corn oil	−15 to −10	117–130	15–19
Rape oil	−10 to −4	94–106	12–18
Castor oil	−18 to −10	81–89	3–5

The word titer is a term applied to the mixed fatty acids that can be obtained from a fat or a soap; it is the temperature at which a liquid mixture of fatty acids will freeze or solidify. It is determined by warming the acids until they have melted, and then cooling the mixture very slowly, stirring, and reading the temperature at which it solidifies. When thinking about titer, you must be careful not to confuse fats with fatty acids. The word titer is not applied to the temperature at which a fat will solidify, but only to the freezing of mixed fatty acids. We shall find that titer values give us much information about the characteristics of a soap.

Most of the figures in Table 6 are taken from *The Industrial Chemistry of the Fats and Waxes* by Hilditch, D. Van Nostrand Company, 2nd Edition, 1941.

The most important chemical property of a fat is the reaction with caustic alkalies, because it is by this saponification reaction that soaps are made. In order to write a chemical equation illustrating this reaction we must use some formula that will represent a fat, and we may as well use stearin as any of the other glycerides

$$\underset{\text{(fat)}}{(C_{17}H_{35}COO)_3C_3H_5} + \underset{\text{(alkali)}}{3NaOH} \longrightarrow \underset{\text{(soap)}}{3C_{17}H_{35}COONa} + \underset{\text{(glycerin)}}{C_3H_5(OH)_3}$$

If the formula for stearin merely represents a fat, then it is seen that glycerin is produced by the saponification of a fat, no matter what fat is used. It is also seen that soap should retain all the characteristics of the long chains of carbon atoms, saturated or unsaturated, which are found in the glycerides.

The presence of double bonds in a fat has a profound effect on its physical form, and that is to lower its melting point very much. For example, both stearin and olein have straight chains of 17 carbons, but stearin is a solid and olein a liquid. The only difference is that olein has one double bond in each chain. We shall also find that these double bonds give special properties to soaps.

The most common method for making soap is known as the boiled and settled method, in which fat is boiled with alkali in large kettles. After saponification is complete a strong salt brine is added for the purpose of separating the soap. After further finishing operations the soap is washed with water until free from caustic alkali. This makes what is known as *neutral soap.*

Some textile operations, such as the milling or fulling of woolens or the degumming of silk, require a very high-grade neutral soap. The expression neutral soap is rather misleading because no soap, no matter how carefully made, is neutral. Solutions of all soaps are alkaline with *p*H (page 381) high enough to turn phenolphthalein red. This is due to the hydrolysis of the soap when dissolved in water. By neutral soap we mean a soap which has been so carefully manufactured that it contains an excess of neither fat nor free alkali. In other words, the fat has been completely saponified and the excess caustic has been completely removed by washing.

For laundry and general utility purposes a neutral soap is not required. In fact, it has been found that soap will be a better detergent and clean better if certain weakly alkaline substances are used with it. Such substances are known as builders or assistants. A built soap is an intimate, uniform mixture of neutral soap and more or less weakly alkaline substances in such proportions that the greatest detergent action and whiteness retention *that are safe for the life and color of washed goods* will be obtained. Detergent action is required for the actual removal of soil from goods. Whiteness retention is connected with the suspending power of the detergent bath, which means its ability to prevent the redeposition of soil on cloth. The consumer may buy soaps that are already built or he may mix the builder with soap as he uses it. Most of the builders are perfectly safe for laundry use provided that they are used judiciously or put into the soap with fairness and judgment. Typical builders are the various sodas, phosphates, and silicates, some of which are shown in Table 7, together with the pH of their solutions at three different dilutions.

The efficiency of various builders, as far as detergent action is concerned, has been studied in many laboratories. For example, Snell[1] found that the efficiency (as aiding detergent action), in decreasing order, was sodium orthosilicate, sodium metasilicate, soda ash blend, sodium hydroxide, modified soda, and soda ash. Morgan[2] found the order to be sodium metasilicate, soda ash, trisodium phosphate, and sodium hydroxide. Vaughn and Vittone[3] found it to be PB 3,[4] sodium hydroxide, PB 2, PB 1, sodium metasilicate, sodium carbonate, trisodium phosphate, modified soda, and sodium bicarbonate.

Study of whiteness retention in connection with builders shows that soap baths, without any builders, are the best. If builders are used the order of efficiency, in decreasing order, is shown to be[4] PB 2, PB 1, modified soda, sodium bicarbonate, trisodium phos-

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[1] *Ind. Eng. Chem.*, **25**, 162, 1240 (1933).

[2] *Can. J. Research*, **8**, 429 (1933).

[3] *Ind. Eng. Chem.*, **35**, 1094 (1943).

[4] PB = proprietary builder, a mixture of silicates and phosphates. Wyandotte Chemicals Corporation.

TABLE 7

*p*H VALUES OF SOLUTIONS OF SOAP BUILDERS IN THREE DILUTIONS AT 25° C*

Salt	Concentration, %	*p*H
NaOH	1.0	13.04
	0.1	12.29
	0.01	11.30
Sodium orthosilicate $Na_4SiO_42H_2O$	1.0	12.81
	0.1	12.01
	0.01	11.00
Sodium sesquisilicate $Na_3HSiO_4 \cdot 5H_2O$	1.0	12.68
	0.1	11.79
	0.01	10.69
Sodium metasilicate $Na_2SiO_3 \cdot 5H_2O$	1.0	12.44
	0.1	11.55
	0.01	10.55
Trisodium phosphate $Na_3PO_4 \cdot 12H_2O$	1.0	11.99
	0.1	11.31
	0.01	10.29
Tetrasodium pyrophosphate $Na_4P_2O_7$	1.0	10.17
	0.1	10.03
	0.01	9.50
Sodium tetraphosphate $Na_6P_4O_{13}$	1.0	8.03
	0.1	8.69
	0.01	8.82
Na_2CO_3	1.0	11.26
	0.1	10.94
	0.01	10.40
$NaHCO_3$	1.0	8.18
	0.1	8.43
	0.01	8.28

* *Ind. Eng. Chem.* **35,** 1289 (1943).

phate, sodium metasilicate, PB 3, sodium carbonate, and sodium hydroxide.

Builders should be blended with neutral soap so that the best detergent and whiteness-retention action is obtained. There is no conventional proportion of builders in soap. Some soaps contain 5%, some 40%, and the optimum percentage depends on the type of work to be done by the soap. Equal detergent improvement can be obtained with any of the accepted builders. It is simply a matter of finding the proper ratio of soap to builder. If the consumer is to use a built soap, he should determine by trial whether the performance of a soap is satisfactory and then balance the costs of two or more such soaps against each other. A chemical analysis of the built soap will not always predict the performance.

PHYSICAL PROPERTIES OF SOAP

There are two general types of soap: (*a*) the soft soaps, potash soaps, which are potassium salts of the higher fatty acids and are usually soft and pasty; and (*b*) the hard soaps, soda soaps, which are sodium salts of fatty acids and are much harder and firmer. Potash soaps find some uses for special purposes, but because of lower cost, and in many cases equally satisfactory performance, the soda soaps are manufactured and used in much greater quantities. Subsequent discussions of the properties of soap in this book will be confined to the soda soaps.

The solubility of a solid is a property that is often passed over or considered too casually. This is a mistake, because the matter of solubility may be an important determining factor in the suitability of the solid for useful purposes; this is particularly true for soap. In order for soap to do any cleaning it must be soluble in water, and if the cleaning is to be done at low temperatures the soap must be soluble in cold or lukewarm water. Furthermore, it should not take too long a time to dissolve, for a soap that dissolves quickly is invariably preferred by the consumer. On the other hand, if a cake of toilet soap is to last well it should not dissolve too easily. For most textile purposes the soap with good solubility is the most desirable.

Another factor must be considered in connection with soap solubility. After a soap has been used for scouring, washing, laundering, or any other purpose, it must be rinsed off, and perhaps one of the most important factors in the performance of a soap is the ease and completeness with which it can be rinsed off. This is particularly true when soap is used with the protein fibers, wool and silk, because small residues of soap left on the goods may cause serious trouble in subsequent processing. These soap-covered areas will resist some kinds of dyes, so that the goods will come up unlevel and spotted. If acid dyes are to be applied, the acid in the dye bath will react with the soap and liberate greasy fatty acids which will prevent the dyeing of those areas, or if the acids separate and float on the surface of the bath they may be picked up by the goods and form oil spots. One of the most common results of soap residues left on wool or silk after washing is the production of bad odors after the goods are stored. It is perfectly obvious that, the more easily soluble a soap is, the more readily it can be rinsed off. That is, there is a direct connection between solubility and rinsibility. This is especially important when cleaning or scouring and rinsing must be done at low or lukewarm temperatures.

We have already said that the characteristics of a soap will depend on the nature of the fat from which it is made. A soap made from a hard fat like tallow, or a fat with a high percentage of solid glycerides in it, will yield a soap that is hard and firm, that will dissolve slowly, and that will be difficult to rinse out. Such a soap would require hot water to dissolve it, and when such solutions are cooled they set to stiff jellies. On the other hand, a soap made from a liquid fat like olive oil will be softer, will dissolve more easily, will not set to a gel as readily, and will rinse off more easily. Still better than this are the soaps made from specially prepared oleic acid.

One of the outstanding properties of soap solutions is their ability to form suds when shaken or agitated. This is due to the fact that agitation permits air to enter the surface of the solution, and small volumes of air become surrounded by films of soap solution to form an air-water emulsion. Soapsuds therefore consists of thousands of little soap bubbles filled with air. When soap is used in laundering, the suds does very little of the real cleaning but it has a definite function that we shall discuss when we study the mechanism of detergent action. We may say at this point that a good stand of suds should be maintained in order to do thorough washing. The sudsing power of a soap, like its solubility and rinsibility, is governed by the nature of the fat or fatty acids used in its manufacture. Hard fats like tallow will make a soap that will form thick stiff suds that will stand up well at high temperatures, whereas a liquid fat or oleic acid soap will make softer, finer, more compact suds at lower temperatures, but the suds tends to break at higher temperatures.

We have learned that the solubility, rinsibility, and sudsing characteristics of a soap are definitely determined by the kind of fat or fatty acids used to make it. But the consumer does not know what fat or mixture of fats has been used to make the soap in which he is interested. He must therefore depend on certain values determined by laboratory examination. One of the most important of these values is the titer of the soap acids. The word titer has already been defined (page 58), but we often find it being wrongly used. We read about a low-titer soap, or a high-titer soap, or a soap made from a low- or high-titer fat. Such use of the word is incorrect, because the word titer refers to the solidifying point of the soap acids (the mixture of fatty acids which can be obtained from the soap) and not to the soap or the fat. In order to determine titer the soap must be dissolved in water and then acidified with a strong acid such as sulfuric acid, whereupon the mixed fatty acids are liberated and, being insoluble and lighter than water, will separate as a layer floating on the surface of the acid solution. These acids must then be washed and dried, after which the titer may be determined. This is done by putting the acids into a 1-in. test tube provided with a loosely held thermometer which dips into the acids. They are then melted, and the tube is suspended in a larger tube (an air jacket) and allowed to cool slowly, with mild stirring. When the mixture begins to get cloudy (the appearance of a solid phase) the tube is allowed to stand without stirring. The temperature will go down below the real solidifying point (supercooling) and then will rise, and the highest point to which it rises will be the titer temperature. If no cloudiness appears in a reasonable length of time at room temperature it means that the titer is lower than 20° C and that the tube containing the liquid mixed acids should be transferred to an ice-water bath. Low-titer acids are those that solidify between 10 and 20° C, whereas high-titer acids solidify between 24 and 45° C.

In the general formula for a soap, RCOONa, the R part may contain from 7 to 17 carbons, and it may be saturated or unsaturated with one or more double bonds in it. The effect of such variations will be found in the titer of the soap acids. As the molecular weight increases, the titer goes up. Therefore the fatty acids from low-molecular-weight fats will have low titers, but fatty acids from a fat like tallow, containing high-molecular-weight glycerides, will have a high titer. The effect of unsaturation is even more marked. Stearic acid, $C_{17}H_{35}COOH$, is a higher-molecular-weight saturated acid and is a solid melting at 69° C. Oleic acid, $C_{17}H_{33}COOH$, has the same number of carbons and practically the same molecular weight, but it has one double bond in the long chain. The effect of this double bond is to make oleic acid a liquid at room temperature and to lower its freezing point to about 14° C.

Soaps that yield low-titer acids are usually easily soluble, even at ordinary temperature, and will form suds in cold water, but the suds will not stand up well at high temperatures. As a rule, smaller amounts of such soaps are required to form a washing suds. Because of their good solubility, they are easily rinsed off goods with cold water. Such soaps are specially suitable for washing woolens, silks, and rayons, where low-temperature washing and good rinsing are essential.

Soaps that yield high-titer acids make up the large family of laundry soaps. They usually require hot water for dissolving them, and when such solutions are cooled a gel is formed. They do not suds easily at low temperatures, but yield good firm suds when heated, and these suds are quite stable. More rinsing is needed to remove such soaps from washed goods, and a hot rinse is much more efficient. They are suitable for washing cottons and linens and for general cleaning purposes.

CHEMICAL PROPERTIES OF SOAP

The chemical behavior of soap in water solution depends on the fact that soap is a salt of a high-molecular-weight fatty acid (a salt of a strong base and a weak acid). We shall discuss only three chemical properties of soap: the reaction with strong mineral acids, the reaction with inorganic salts, and hydrolysis.

When a salt of a weak acid is subjected to the action of a strong acid the weak acid is liberated, and since soap is a salt of high-molecular-weight fatty acids, which are very weak acids, these acids should be liberated when soap is treated with a strong acid. This is shown by

$$C_{17}H_{35}COONa + HCl \longrightarrow C_{17}H_{35}COOH + NaCl$$

$$C_{17}H_{33}COONa + HCl \longrightarrow C_{17}H_{33}COOH + NaCl$$

Not only are these high-molecular-weight acids very weak, but they are insoluble in water, so that they will be precipitated when soap is treated with HCl. However, the word precipitated is hardly correct, because it usually is associated with the formation of a solid that settles to the bottom of a reaction mixture. In the first of the above equations, the acid, stearic acid, is a solid, but it is not a crystalline solid nor is it heavy enough to sink to the bottom. The solid high fatty acid separates in the form of flakes which get together to form curds, and since the curds are lighter than water they will float on the surface of the acidulated solution. In the second equation, the acid, oleic acid, is a liquid at ordinary temperature, and since it is lighter than water it will float on the surface in the form of an oily layer. As soaps are salts of mixtures of fatty acids, the nature of the separated fatty acids will depend on the fat from which the soap was made, soaps made from hard fats yielding a fairly firm solid mixture of fatty acids, and soaps made from liquid fats yielding an oily mixture of fatty acids.

This reaction between soap and mineral acids is very important in textile technology. When goods are scoured or boiled off, small residues of soap may escape rinsing and be left on the goods, both on the surface and the interior of yarns. If the goods are later subjected to some acid processing (such as the dyeing of wool with acid dyes or the brightening of silk with acid), free fatty acids will be deposited at such points, and this may be quite objectionable. The reaction between soap and mineral acid is used to liberate the mixed fatty acids so that the titer can be determined (see page 58).

The reaction between soap and inorganic salts is responsible for some of the greatest problems in the textile industry. The sodium, potassium, and ammonium salts of high fatty acids are the only ones that are soluble in water, and even so their solubility is not very great. Hence, according to the old law of solubility product, whenever soap comes into contact with any other cations an insoluble soap will be precipitated. This most commonly occurs when soap is used with hard water. Hard water contains soluble calcium and magnesium salts, such as $CaSO_4$ and $MgSO_4$, which react with soap.

$$2RCOONa + CaSO_4 \longrightarrow (RCOO)_2Ca + Na_2SO_4$$

Whenever textile materials are washed in hard water these insoluble soaps will be formed and will be deposited on the goods. As these metallic soaps are insoluble in water, they can do no cleaning whatever. In other words, soap that is precipitated in this way is wasted as far as cleaning is concerned. The actual cost of such wasted soap is not so great, but the real cost is measured by the trouble caused by the insoluble soaps thus formed. A discussion of these troubles is found on page 87. It is a common experience to find an insoluble, greasy scum on the surface of hard water in which soap has been used. This scum is a mixture of calcium and magnesium salts of high fatty acids.

There are some peculiarities in the manner in which insoluble soaps are separated from hard-water solution. The separation seems to depend on the relative amounts of soap and mineral salts in the water. If a large excess of soap is used (as in the boiling-off of silk), the insoluble soaps are formed in a very finely divided condition, so that separation, in the sense of settling out or coming to the surface, does not occur. However, if a small amount of soap is used with hard water the insoluble soaps form in flakes, some of which unite to form curds and come to the surface. This would be the situation when goods washed with soap are rinsed with hard water: a small amount of soap is left after whizzing or wringing. There are some phosphates and silicates (such as sodium tetraphosphate, Quadrafos) that will remove deposits of lime soaps and regenerate the soda soap.

Three types of salts hydrolyze when dissolved in water: salts of strong bases and weak acids, strong acids and weak bases, and weak acids and weak bases. Soap belongs to the first type, and when it is dissolved in water the following reaction takes place:

$$\mathrm{RCOONa} + \mathrm{HOH} \rightleftharpoons \overline{\mathrm{RCOOH}} + \mathrm{Na^{+}OH^{-}}$$

This is a reaction in which water takes part chemically and is not just a solvent. You will note that the products of this hydrolysis are an acid and a base, a very weak and not easily soluble acid and a strong, highly ionized base. These cannot exist side by side to any great extent because they will react with each other to form a salt and water, and it should be obvious that a condition of equilibrium will be attained at which point the four compounds will be present. The relative point of equilibrium is designated by the two arrows. Hydrolysis is a spontaneous reaction which cannot be prevented. As soon as soap is dissolved in water it hydrolyzes and increases the [OH^-] of the solution. This is the reason that all soap solutions are alkaline, even solutions of a neutral soap. A neutral soap, *per se*, may contain neither free acid nor base, but as soon as it is dissolved in water the solution will be alkaline enough to turn phenolphthalein pink; that is, the *p*H of the solution will be about 8 or 9. Therefore we can talk about the alkalinity of a soap, not because the soap may contain any free alkalinity, but because it will develop alkalinity when it hydrolyzes in solution. Because of this property of hydrolysis a soap can be titrated, just as sodium carbonate can be titrated, and the total alkalinity can be determined.

There are two main kinds of alkalinity in a commercial soap, combined alkalinity and free alkalinity. Combined alkalinity is due to the soap itself, that is, the potential alkalinity that is combined with fatty acids in the soap. Free alkalinity is due to the presence of alkaline substances other than soap, e.g., free NaOH not removed during the manufacture of the soap, and soda ash or other alkaline builders that have been added intentionally. Free alkalinity is usually expressed in two forms: free caustic alkalinity (due to free hydroxide ions not formed by the hydrolysis of soap), and free carbonate alkalinity (builder alkalinity). The combined alkalinity can also be thought of in two ways: the total combined, that is, the total alkalinity that would result if the soap were 100% hydrolyzed; and the available alkalinity, that is, the alkalinity that is actually developed when the soap hydrolyzes. Methods for the determination of these values may be found in any book on technical methods of analysis of commercial products.

The alkalinities of soap are expressed in terms of Na_2O, sodium oxide. It is true that there is no such thing as a solution of sodium oxide, but the expression is used by common consent because the analyst does not know whether the alkalinity in a soap solution is due to NaOH, KOH, Na_2CO_3, K_2CO_3, or any of the other basic substances that might be found in soap. However, it makes no difference, because the equivalent weights of all alkaline substances have the same alkalinity; that is, they will react with the same weight of some specific acid. A 0.1 *N* solution of NaOH is exactly equivalent to a 0.1 *N* solution of Na_2CO_3 or K_2CO_3 or Na_3PO_4. And so a hypothetical 0.1 *N* solution of Na_2O is also equivalent to any of the above solutions. This may be extended to a soap solution, even though soap is not a definite, pure compound.

In the accompanying chart are found analyses of two typical commercial soaps; all the figures are percentages of Na_2O in the dry soap.

Soap	Total	Free	Total Combined	Caustic	Carbonate
I	9.1	0.51	8.59	0.0	0.51
II	13.56	5.28	8.28	0.3	4.98

We are interested in the amount of hydrolysis of different types of soap, soaps made from hard fats as compared with soaps made from liquid fats, and soda soaps as compared with potash soaps. McBain[5] found that 0.3% solutions of pure potassium palmitate hydrolyze 6.8%, and 0.3% solutions of sodium palmitate hydrolyze 6.6%. The effect of concentration is shown by the fact that 2.75% solutions of the same soaps hydrolyze 1.25% for the potash soap and 1.0% for the soda soap.

If we compare soaps made from liquid fats with those made from solid fats of the same molecular weight we find that the solid-fat soaps will hydrolyze considerably more than the liquid-fat soaps. That is, sodium stearate hydrolyzes more than sodium oleate. Soaps with mixed fatty acids of lower molecular weight hydrolyze still less. This is one reason that coconut oil is used for making shaving soaps.

DETERGENT ACTION

Many people think that cleaning a soiled surface is a rather simple matter, but this is far from true, as will be seen from a discussion of the following variables involved in any detergent operation:

1. The nature of the dirt.
2. The nature of the surface to be cleaned.
3. The nature of the water.
4. The nature of the detergent.

We shall divide dirt into two classes, on the basis of whether it is soluble or insoluble in water. Soluble dirt may consist of a few organic acids, mineral acids, alkaline substances, blood, starch, sugar, etc., all of which are more or less soluble in cold or lukewarm water. No special detergent problem is involved in the removal of such dirt, because it is merely a matter of getting the dirt into solution and thus removing it from the surface being cleaned.

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[5] *J. Chem. Soc.*, **105**, 957 (1914); **115**, 1279 (1919).

Insoluble dirt is of two types: (*a*) solid mineral matter, such as finely divided siliceous, earthy solids, and dust which need not necessarily be heavy dirt like sand, but may be so fine that it will remain suspended in air for a long time; and (*b*) liquid and solid organic materials such as grease, fats, oils, and waxes. The significant difference between the two types is that one is greasy and the other is not. It is such kinds of dirt that present problems to the home and commercial laundry and require real detergents for removal, because more than mere solution is necessary.

The manner of attachment of insoluble dirt to cloth is one of the most important aspects of general cleaning. The following observations based on common experiences will illustrate this. When a cloth that has collected dust is shaken, much of the dust will be removed, but not all of it; the rest is held on the cloth by fairly strong forces of physical attraction. This leaves the cloth dirty. The same sort of attachment of dirt might be ascribed to the wallpaper above a radiator or register, which becomes dirty much more quickly than wallpaper at any other place in a room. These are examples of dirt that may be held by physical forces, but dirt is held in another way that is perhaps more important. This is due to a combination of the two types of dirt, that is, mineral dirt which is held on cloth by a film of grease or fat. It is well known that collars and cuffs become dirty when the wearer is doing no special work that would cause the dirt, and it is also well known that they become dirty on the inner side, next to the skin, rather than on the outer side.

The conclusion must be that much of the dirt on textile materials is held by a film of oily or greasy matter. With clothing worn next to the skin, the grease comes from the skin. The air is filled with millions of minute particles of mineral and organic matter, dust, soot, smoke particles, etc. These particles come into contact with clothing and are held there by grease films. The dirt on wallpaper above a radiator is probably due to two causes: the mineral particles in the air, held by physical attraction and also held by a very thin grease film picked up by the dust particles from minute oil particles in the air.

The greasy film that holds dirt to surfaces may be of two types: mineral oil, such as machine oil or automobile grease, or grease of the glyceride type, such as fat. Note that these two types of grease differ radically in one important property. Mineral oil cannot be saponified, but the glyceride type of grease is saponifiable. On the other hand, both types have some common properties, only two of which concern us. They are both insoluble in water, and both can be emulsified.

The nature of the surface to be cleaned is an important factor. Some surfaces, such as walls, floors, and dishes, are flat and fairly smooth. But in the textile field we must consider the cleaning of cloth, which really is an intricate and involved material. The type and construction of the cloth determine its capacity for holding dirt, and its capacity for reacting physically or chemically with the detergent solution. A piece of cloth has an exterior surface, but it also has many interstitial, interyarn surfaces which can hold dirt particles. We often speak of dirt that is "ground in," meaning that the dirt has been forced in between the yarns of the cloth. Furthermore, it may get in between the individual fibers of the yarns. Actually a cloth consists of a mass of large and small capillaries, and the dirt is partly on the exterior surface and partly on the walls of these capillaries. Any detergent must be able to penetrate these capillaries and wet their walls in order to remove dirt.

The nature of the fibers is also an important factor. A rough fiber will tend to hold dirt more tenaciously than a smooth fiber. Thus rayon and nylon will hold dirt less easily than cotton or wool, and mercerized cotton will not soil as quickly as unmercerized cotton. Some fibers, such as wool, because of their chemical nature, will selectively absorb the alkaline part of soap and deposit fatty acids on the cloth. It is interesting to note that the newer detergents (Gardinols, etc.) have no alkali available for selective absorption by the cloth.

It is common knowledge that hard water is not good for laundering because of the formation of insoluble calcium and magnesium soaps. The newer detergents will form clear solutions with water, and there is a very large reduction in the amount of insoluble matter deposited on washed goods.

The fourth variable involved in a cleaning operation is the nature of the detergent. For many years soap has been considered the universal detergent, and the present discussion will attempt to explain why. Before doing this it is necessary to discuss three additional physical properties of soap that are vitally connected with its detergent property: its emulsifying property, its ability to lower the surface tension of water, and its ability to lower the interfacial tension between water solutions and solid objects.

An emulsion is a dispersion of one nonmiscible phase in another. If two immiscible liquids are vigorously shaken together, the one present in the smaller amount will be broken up into fine particles, each of which will be surrounded by particles of the other liquid. This is an emulsion. In other words, an emulsion in this instance is a system consisting of finely divided particles of one liquid dispersed in another liquid that is immiscible with the first one. The first liquid is known as the *dispersed phase*, and the second liquid is called the *dispersion medium*. Most emulsions will break after a period of time; some of them break quickly, and others stand up for a long time. Whole milk is a good example of an emulsion, and the gradual separation of cream is the result of the breaking of the emulsion. When this happens, finely divided particles of cream coalesce to form a separate liquid layer. Small amounts of grease or oil can be dispersed in water by means of sufficient agitation to form an oil-in-water emulsion, but as a rule only small amounts of oil can be emulsified in this way, and because the emulsion is not stable it will break very quickly and separate into an oil layer and a water layer. The amount of oil that can be emulsified, and the stability of the emulsion, can be increased by the use of an emulsifier or emulsifying agent, and we find that soap is such an agent. Since the detergent action of soap solutions is based primarily on the ability of soap to emulsify grease or oil, we must investigate the reasons for this function. A description of a few simple experiments and the observations made from them will help to explain why soap is a good emulsifying agent.

It is possible to place a clean needle on the surface of water so that it will not sink. Picture in your mind this needle, which is heavier than water, floating on the surface of water. What holds it up? What prevents it from sinking? It is a physical property of water known as *surface tension*, a property concerned only with the surface layer of the water or the surface of a drop of water. *The surface tension of a liquid is a force that resists attempts to* *increase the area of the surface of the liquid.* Consider the surface layer of water as a film or a kind of skin having within itself a force that fights to keep the area of the skin or film from being increased or stretched. When the needle is placed on the surface of water, being heavier than water, it tends to sink, but before it can do that it must break through the skin that constitutes the surface layer of the water. The needle would have to push down on the surface and stretch it until it breaks and lets the needle through. The force called surface tension resists this stretching up to a certain point. In our experiment with the needle and water this resistance is great enough, and the needle does not sink. In other words, water has a relatively high surface tension. The needle will not float on the surface of alcohol or benzene, because the resistance offered by the surface tension of these liquids is not great enough. They have lower surface tensions than water.

The magnitude of the surface tension force varies not only with the nature of the liquid itself but also with the temperature, and it can be changed by the addition of other substances. Soap is one of the best substances known for lowering the surface tension of water, and this factor plays an important part in the detergent value of soap. A needle will not float on the surface of water after soap has been dissolved in it, which means that the surface tension of the water has been lowered and the resistance to an increase in area has been reduced. This is illustrated further by the fact that you cannot blow a bubble with water but you can with soap water, and it is perfectly evident that the surface of the soap bubble has been stretched and that its area is enormously larger than the surface of the soap water taken up by the bubble blower. Lowering of the surface tension of water is a property of all detergents or emulsifiers.

Table 8 gives the surface tension of a few liquids and shows how the value changes with temperature. The values are expressed in dynes per centimeter.

Table 9 shows the relative surface tension of solutions of various detergents as compared with water = 1.0. It is seen that quite a small amount of detergent lowers the surface tension of water very appreciably, but that nothing is gained by using concentrations greater than 0.2%.

In order to appreciate the significance of a low surface tension consider an observation that everyone has made at some time or other. You have seen drops of water on a greasy surface and noted that they stand up like balls and tend to retain their spherical shape. Why do they not flatten out? Because, if they did, it would necessitate an increase in the areas of their surfaces, and the force of surface tension resists this change. Now if you were to place drops of soap solution on this same greasy surface you would discover that they would not stand up like balls, but would flatten out because the surface-tension-resisting force of the water is no longer as great as it was. Which form, the ball form or the flattened-out form, would cover the larger area of the greasy surface? Which form would wet the larger area? It is perfectly obvious that the drops of soap solution would wet the greater

TABLE 8

Surface Tension

Temperature, ° C	Water	Alcohol	Benzene
0	75.64	24.05	31.58
20	72.75	22.27	28.88
25	71.1	.....	.....
35	70.0	.....	.....
40	69.56	20.60	26.26
60	66.18	19.01	23.72
70	64.42	18.22	22.48
90	60.75	.....	.....
100	58.85	.....	.....

TABLE 9

Relative Surface Tension of Solutions

	Relative Surface Tension; Water = 1.0			
Percentage of Material in Solution	Sodium Palmitate at 25° C	Igepon at 35° C	Dreft at 35° C	Polyglycerol Ester at 35° C
0.01	0.7	0.80	0.80	0.69
0.05	...	0.52	0.48	0.44
0.1	...	0.44	0.45	0.40
0.15	0.3	0.42	0.42	0.39
0.2	...	0.41	0.41	0.39
0.3	...	0.41	0.41	0.40

area, and the term wetting power is used to describe this fact. If cloth is substituted for the greasy surface, the same relations hold true, i.e., soap solution wets cloth better than water does. This also means that it will penetrate better and be soaked up faster. In this way the soap solution can get under the grease film holding the dirt on a fabric and loosen it better than water can. The importance of the lowering of surface tension of water in connection with laundering should be apparent.

Another tension also plays a part, namely, *interfacial tension.* Recall the needle experiment. As long as the needle floats on the surface of the water it is not wetted but merely rests on the surface film. If a force acts upon it so as to push it through the surface and into the main body of the water, then it is wetted, and it becomes wet because there is an attraction force between the water particles and the needle. They tend to stick together. An object is said to be wet when the surface (or face) of the object and water particles have enough attraction for each other so that they are compatible and stay together. If such an attraction did not exist, the water would fall off the object and it would not be wet. Interfacial tension is the force that opposes this attraction or wetting effect so that, if this tension is reduced in some way, the two will come into contact with each other and the solid object will be wetted more easily. When soap is dissolved in water the interfacial tension between water and cloth is lowered.

This action can be demonstrated by dipping one piece of heavy cotton cloth in water and another piece of the cloth in soapy water. The second cloth will be found to be much wetter than the first. The addition of soap to water also lowers the interfacial tension between water and oil, and for this reason an oil-soap-water emulsion will be more stable than an oil-water emulsion. We also conclude from this that soap solutions are good wetting and penetrating agents, as any detergent must be. A good soap in solution will have a low surface tension against air and a low interfacial tension against an oil or a piece of cloth.

Soap solutions will form emulsions not only with oil but also with air. When a soap solution is shaken, suds are formed consisting of tiny volumes of air entrapped or surrounded by films of soap solution. This is an air-soap solution emulsion. Its importance in detergent action will be discussed later.

Consider how a soap molecule is constructed. It consists of two parts, an ionizable salt part (—COONa) and a long-chain hydrocarbon part ($C_{17}H_{35}$—). The salt end of the soap molecule behaves like any sodium salt in that it is much more soluble in water than it is in oil. On the other hand, the long carbon chain part of the soap molecule acts like a hydrocarbon in that it is much more soluble in oil than in water. You may think of a soap molecule as a snake with a water-soluble head and a fat-soluble body. Such a chemical snake would have what we might call an unsymmetrical duality of affinity; the head has an affinity for (or is attracted by) water, and the body has an affinity for (or is attracted by) oil. Some of the physical properties of soap solutions can be explained on the basis of this duality of affinity: the low solubility of soap in water at low temperatures and the large increase in solubility above certain critical temperatures; the colloidal nature of soap solutions; the formation of micelles, long bundles of parallelized molecules held together by the attraction of the water-repelled hydrocarbon chains for each other; and the lowering of water-oil interfacial tension.

Let us consider how soap molecules may arrange or orient themselves in the surface layer of a dilute soap solution, not in the interior of the solution but only on the very surface of it. The salt heads of the molecules are soluble in water, but the long carbon chain bodies are repelled by water, just as oil is repelled and not attracted by water, and so they are left protruding above the surface film of water. You may picture the surface of a soap solution as filled with snakes, their heads buried in the surface and their bodies waving around in the air. What will happen when such a surface comes into contact with a greasy surface? The exposed hydrocarbon chains will not be repelled by this surface but instead will be attracted to it because they are soluble in grease. The heads of the snakes remain in the water and the bodies are imbedded in the grease, and we can say that the interfacial tension has been lowered to such an extent that the greasy surface has been wetted with the soap solution. Thus the surface layer of soap molecules acts as a binder or a uniting link between water and grease. It is seen that if such a system were to be shaken the grease might break up into small particles and each would be surrounded by soap molecules so that an emulsion would be formed. This mechanism not only aids in the formation of an emulsion but also increases its stability, because it would be difficult for the small oil particles to get together and form a large globule or an oil layer.

It is found that the hydrocarbon end of soap must contain several carbons. Sodium acetate, in which the chain consists of only one carbon, will not form oil-water emulsions or suds, nor has it any detergent action. These desirable properties become apparent when the average chain length of a soap is 10 or 12 carbons.

Let us now briefly consider the detergent action of soap solutions and the general problem of washing. We must remove dirt that is held in two different ways, and in both instances the dirt particles must be loosened from the surface. If the particles are held by physical attraction (no grease film) they can be loosened by agitation with water to which soap has been added, thus lowering the interfacial tension between water and dirt particles.

In order to loosen dirt particles held by an oil film it is necessary to emulsify the oil or grease. If we have a theory for removing one particle, then we can remove thousands in the same way. Soap solution is brought into contact with the dirt; the surface of the grease is wetted; agitation produces soapsuds and a grease-water emulsion; the grease is entrapped by soap particles; the particle of mineral matter is set free. It is seen that all these things depend on a surface phenomenon, and the only portion of soap that takes part in the cleaning is the part in the surface adjacent to the dirt. Also note that the soap solution does not act on the mineral particle itself but only on the film of grease surrounding and holding the particle.

After dirt particles have been loosened and removed from cloth they must be prevented from reattaching themselves. If they are heavy particles they will sink to the bottom of the water. The light particles will be held in suspension, mostly in the soap solution but to some extent in the suds. Here again soap plays an important part, because it lowers the water-dirt interfacial tension. Furthermore, the emulsified grease must be prevented from separating and becoming attached to the surface being washed. The good emulsifying property of soap accomplishes this, since the oil-water-soap emulsion is fairly stable.

Now let us consider the removal of dirt from a piece of cloth. The cloth consists of an outer surface and a mass of large and small capillaries in the interior of the cloth, and these capillaries are filled with air. The dirt is found on the outer surface and is also deeply imbedded among the individual fibers. Soap solution is a good penetrating, wetting, and emulsifying agent, and so when the cloth is washed the soap solution penetrates the capillaries, emulsifies the air in them, wets their walls, and removes the dirt by emulsifying the grease that holds it.

THE NEW DETERGENTS

We have pointed out that soap is a good detergent and also a good wetting agent, but we know too that there are serious objections to its use and faults to be found with it. One of the main objections is its curd-forming property with hard water. Translated into chemical terms, this is due to the very slight solubility of the calcium, magnesium, and iron salts of the high fatty acids. That is, if calcium stearate were soluble in water it would not appear as a curd or scum. We have found that, when soap is used with hard water, part of the soap is precipitated by the hardness and is not available for detergent action. In other words, part of it must be used to soften the water. It is not at all uncommon to find 50% of the total soap used for cleaning wasted in this way. Not only do we have this economic objection, but we object to the slimy curd sticking to the sides of vessels and to goods being cleaned. It is difficult to rinse off the curd, and the goods come out with a poor appearance. Another objection is that soap is decomposed by acids. This is not so important a factor to the average user of soap, but in the textile industry there are many operations, such as dyeing, in which a good wetting agent is desired, but it must be one that will stand up in the presence of acid in the bath. Soap cannot be used for such purposes.

The first effort to supply a wetting and detergent agent that could be used with hard water or acidulated water was made by sulfonating castor oil with concentrated sulfuric acid. The product is known as Turkey-red Oil. It is not a substance of very well-defined chemical composition, but for all practical purposes its formula may be given as $C_{17}H_{32}(SO_4H)COOH$; that is, there is a carboxyl group on the end and an acid sulfate group near the middle of the long chain of carbons. The disodium salt of this compound was used. It was a good wetting agent and was fairly inactive toward acid and hard water, but its detergent property was quite poor, so that it really did not take the place of soap. It was considered necessary to get rid of the carboxyl group (or the COONa group), and so various changes were made. The COOH group was esterified and also converted into an amide (in both cases leaving the acid sulfate group intact), but very little improvement resulted. It was finally decided that the carboxyl group must be removed and the acid sulfate group put at the end of the long carbon chain.

The manufacture of such compounds is protected by several patents, but in general the procedure is as follows. Suitable fats (fats with the proper carbon chain length) are hydrolyzed to fatty acids; the fatty acids are hydrogenated with hydrogen gas at about 300° C under a pressure of about 100 atmospheres, in the presence of a catalyst such as finely divided nickel, to form a high-molecular-weight alcohol, such as $C_{12}H_{25}OH$. Obviously, if the raw material is a fat (a mixture of glycerides) it will yield a mixture of alcohols. This mixture can be separated by fractional distillation. Coconut oil is one of the fats used in large amounts for making such alcohols because the lower-molecular-weight alcohols can be distilled off, leaving those with an average hydrocarbon chain of 12 carbons, which we may represent by lauryl alcohol, $C_{12}H_{25}OH$. The next step is to convert this alcohol into its sulfuric acid ester, by treatment with strong sulfuric acid under controlled temperature conditions.

$$C_{12}H_{25}OH + H_2SO_4 \longrightarrow \underset{(C_{12}H_{25}SO_4H)}{C_{12}H_{25}OSO_2OH}$$

Since lauryl hydrogen sulfate has an acid-replaceable hydrogen it can be converted into its sodium salt, $C_{12}H_{25}SO_4Na$, and we now have a compound that satisfies all the requirements of a detergent. One end of the molecule is a water-soluble, ionizable group, —SO_4Na, and the rest of the molecule is a long hydrocarbon chain. These hymolal salts, sodium salts of high-molecular-weight alcohol acid sulfates, are known as Gardinols. The name Gardinol is a generic term applied to the sodium salt of any alkyl hydrogen sulfate. In this country one of the best-known examples is Dreft.

These Gardinols are marketed as the sodium salts, white solids which are more crystalline than soap. Some of their more striking characteristics are:

(*a*) At suitable temperatures they are not affected by hard water.

(*b*) They show a neutral reaction both in solid form and in solution. A water solution containing about 0.1% Gardinol will have a *p*H of about 7.5.

(*c*) They are stable in alkaline solution (that is, they are not hydrolyzed easily), and they retain their soaplike properties when mixed with substances such as soda ash.

(*d*) They are good wetting agents in acid solutions. They are slowly decomposed by acids, but the rate of decomposition is so slow that little trouble is caused.

Hymolal salts of three alcohols are on the market. They are not salts of one alcohol only, but cover a narrow range. For example, the first one produced commercially was made from alcohols obtained by high-pressure hydrogenation of tallow, yielding alcohols containing from 16 to 18 carbons. Another one is made from sperm oil and contains some unsaturated carbon chains.

The most important hymolal salt is made from coconut or palm oil and is marketed as the sodium salt. It contains from 10 to 14 carbons and might be represented by the formula for sodium lauryl sulfate, $C_{12}H_{25}OSO_2ONa$. When sold in bulk quantities to the textile trade it is called Gardinol WA, and when sold in bulk to the nontextile consumer it is called Orvus. For the general public it is packaged and called Dreft. Some of its properties are:

(*a*) It is more easily soluble than soap.

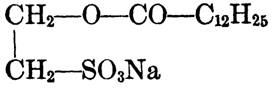
(*b*) It requires a smaller amount than soap to produce suds.

(*c*) It will not precipitate with magnesium or iron ions, and at temperatures above 35° C it will not precipitate with calcium ion. This means that it can be used generally with hard water without producing a scum.

(*d*) It can be used with sea water or other waters having a high salt content, whereas soap is unsuitable for such purposes.

(*e*) Because it is not sensitive to hard water, the amount required in laundering is independent of the hardness of the water.

Another type of detergent, known as Igepon, has a terminal sulfonate group. There are two classes of Igepons, the ester type and the amide type. These are long-chain esters or amides in which a sodium sulfonate group is substituted in the alcohol part of the ester or on the nitrogen of the amide. The ester type of Igepon can be represented by



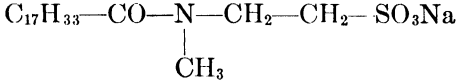
$$\begin{array}{l} CH_2-O-CO-C_{12}H_{25} \\ | \\ CH_2-SO_3Na \end{array}$$

This might be considered a derivative of ethylene glycol, $HOCH_2—CH_2OH$, in which one of the OH groups has been sulfonated and the other has been esterified with a fatty acid in order to secure the attachment of the long carbon chain, which is essential.

The amide type of Igepon may be represented by

$$C_{17}H_{33}—CO—NH—CH_2—CH_2—SO_3Na$$

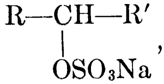
This can be considered a sulfonated alkyl amide of oleic acid. The most important of the amide Igepons is Igepon T, in which the other amide hydrogen is substituted by a methyl group to give



$$C_{17}H_{33}—CO—\underset{\underset{\displaystyle CH_3}{|}}{N}—CH_2—CH_2—SO_3Na$$

The Igepons have properties like the Gardinols as far as their behavior with hard water and stability toward acids are concerned. They are also similar in the sense of their detergent potentialities because they both have long-chain, surface-active anions.

Another group of new detergents has been developed, the members of which have long-chain surface-active cations. This group can be represented by cetyl pyridinium bromide, $C_{16}H_{33}N(C_5H_5)Br$; cetyl trimethyl ammonium chloride, $C_{16}H_{33}N(CH_3)_3Cl$; and Sapamine, which is something like the amide Igepons, $C_{17}H_{33}CO—NH—CH_2—N(C_2H_5)_2HCl$. These detergents have certain disadvantages, as they form precipitates with ordinary soap as well as with other long-chain anions.

Other synthetic detergents and wetting agents that have good dispersing properties and do not permit calcium soaps to deposit on the goods are Teepol X, which is a secondary alkyl sulfate of the type  $\underset{\underset{\displaystyle OSO_3Na}{|}}{R—CH—R'}$, and some of the Tritons, which are aryl alkyl polyether sulfonates. These products are not affected by acids or alkalies and can be used with soap and hard water. For example, Teepol X can be used in a hard-water rinse after goods have been washed with soap, and it will disperse the calcium soaps so that they can easily be rinsed off.

Similar synthetic detergents are Aerosol OT, which is a dioctyl sodium sulfosuccinate; Duponol PC, which is a mixture of the sodium salts of alkyl sulfates with chains of 8 to 18 carbons; and Nacconol N.R.S., which is a sodium alkyl benzenesulfonate mixture.

Another type of detergent, which has been developed by Lever Brothers, is based on the partial esterification of polyglycerol. When glycerin is fully esterified with higher fatty acids, the product is ordinarily insoluble in water and has no emulsifying property, so that it would be useless as a detergent. However, glycerin can be polymerized, and if this polyglycerol is partially esterified with coconut oil fatty acids and mixed with sodium metaphosphate, sodium pyrophosphate, and sodium sulfate, a powder solid detergent is produced which is soluble in water, has good detergent properties, will emulsify fats, and will not precipitate with hard water.

When glycerin is heated to 250–300° C in the presence of a catalyst such as sodium hydroxide, a condensation type of polymerization takes place. The following equation shows the formation of a dimer of glycerin:

$$CH_2OH—CHOH—CH_2OH + HOCH_2—CHOH—CH_2OH$$

$$\longrightarrow CH_2OH—CHOH—CH_2—O—CH_2—CHOH—CH_2OH + HOH$$

Such a polymer can be partially esterified with a high-molecular-weight acid to form a compound such as

$$CH_2OH—CHOH—CH_2—O—CH_2—CHOH—CH_2O—CO—C_{11}H_{23}$$

Washing preparations can be made from polymers ranging up to decaglycerol, but it has been found that the esters of pentaglycerol are the best detergents. Therefore, with proper control, glycerin is polymerized to the pentamer and then esterified with coconut oil fatty acids at 240–250° C. In order to obtain a preponderance of the monoester, only about 10 to 20% of the fatty acids that would be required for complete esterification is used. The chief difference between the polyglycerol esters and Gardinols or Igepons is that the esters are not ionized. For this reason they cannot form insoluble compounds with hard water, nor are they sensitive to mineral acids or any of the agents used in cleaning or processing cloth. One advantage they have over the ionizable detergents is that there is no chance for any preferential absorption of any part of them by any fibers.

These detergents are equal in their ability to lower the surface tension of water and to lower the relative interfacial tensions. They also leave about equal amounts of mineral and fatty matter on cloth after it is washed in them. When used on wool, they all give more satisfactory results at temperatures of 40° C or lower.

QUESTIONS

1. Name some common raw materials from which soap is made.

2. What is the difference between a so-called hard soap and a soft soap?

3. To what does the word titer refer?

4. Write formulas for stearin and olein. Which one would make a hard, stiff soap?

5. What is the relation between unsaturation in a fat and (*a*) whether it is a liquid or a solid; (*b*) the properties of a soap made from it, such as solubility, sudsing power at low temperatures, and stability of suds at high temperatures; (*c*) the titer of mixed fatty acids obtained from it; and (*d*) its iodine value?

6. How can the relative unsaturation of two fats be determined?

7. What is the purpose of a soap builder? Name some soap builders.

8. What is the advantage of having the builder incorporated in the soap as compared with using it separately?

9. Why would you not use calcium hydroxide as the alkali for making a laundry soap?

10. About how much soap can one dissolve in a liter of water?

11. What is meant by a neutral soap? How does a solution of neutral soap behave with phenolphthalein? Explain your answer.

12. In what way are the animal and vegetable fats like simple esters such as ethyl acetate?

13. What is the main difference between fats and waxes?

14. What is the name of the reaction by which soap is made from a fat? Write a typical equation for it.

15. How does soap react with mineral acids (H_2SO_4)? Give an equation. How do soaps react with mineral salts ($MgCl_2$)? Give an equation.

16. What part of the soap molecule determines its physical properties?

17. What would happen if you washed clothes with soap in softened water and then rinsed them with hard water?

18. Discuss the kinds and source of the alkalinity in soap.

19. What is an emulsion? Define surface tension. What connection is there between the amount of surface tension lowering by soap and its power to form emulsions with fatty materials?

20. Tell how you might demonstrate surface-tension lowering.

21. What is meant by interfacial tension?

22. What causes collars and cuffs to become dirty?

23. State in a few words what must be done to remove this dirt.

24. What are the variable factors in a cleaning operation?

25. Draw a diagram to illustrate the orientation of soap molecules in the surface layer of a soap solution.

26. Discuss the detergent action of soap.

27. What is a typical formula for a Gardinol (Dreft)? How is it made from a fat? How do the Gardinols differ from soap in chemical properties? Are their solutions alkaline? How do they behave with hard water?

28. What are the Igepons?

29. How are the polyglycerol esters made?

4 · Water

Water is one of the most important substances used in the textile industry. Each day millions of gallons of it are used in mills, bleacheries, dyehouses, laundries, homes, etc., in the preparation of raw materials and in all wet processes in the manufacture and maintenance of textile materials. Large volumes of water are required in the scouring, carbonizing, dyeing, fulling, and finishing of wool cloths, in the bleaching, sizing, mercerizing, and dyeing of cotton goods, in degumming and finishing silk, in rayon manufacture, and for other purposes too numerous and well known to mention. The right kind of water is so important that it frequently decides the location of a textile mill, because the mill must be situated near an ample supply of good water. It thus seems proper that we should begin the study of textile chemistry with a discussion of water, its sources and types; the disadvantages of some waters and the removal of objectionable qualities; types of hardness; testing water, etc.

The consumer can choose among three sources for the water he uses: rain water, well water, or river water. These three very general types of water will vary considerably in their composition, as will be seen by the following descriptions. As rain water falls it is quite pure and very soft, the only impurity being a small amount of dissolved gases that it picks up as it passes through the air. The objections one might have against rain water arise from the ways in which it is collected and stored. If it falls on a dirty, dusty roof it will dissolve soluble impurities and collect finely divided particles of insoluble material which may stay in suspension for a long time or form a sludge in the storage tank which will be stirred up easily when the water is pumped out. The cistern or tank in which rain water is stored should be cleaned frequently to prevent the transfer of various kinds of dirt to the water.

Well water is rain water that has passed through a little more complicated procedure before it is stored. As rain falls on the ground, some of it runs off and some of it sinks into the ground. As the water travels down through loose soil it dissolves some of the minerals of the soil and thus becomes hard. However, it has very little suspended matter in it because some strata of the soil act as filters and remove the finely divided solid matter. It finally reaches some rocky impervious pocket or chamber which acts as its storage place and from which it can be pumped. The amount of mineral matter that the water will dissolve, and hence its degree of hardness, depends on the types of soil through which it passes. Water that seeps through a limestone deposit will dissolve a large amount of mineral and become very hard, whereas water that passes through a granite-like solid will not dissolve so much mineral matter and will be only moderately hard.

Rain water that runs off the soil and finds its way into a stream does not have much time to dissolve minerals and therefore will be a soft water. However, as it runs off it carries with it small particles of solid material, usually humus-like organic matter, which means that the water will have considerable suspended matter in it. Several factors determine the degree of hardness and suspended matter in river water: type of soil over which rain water passes on its way to the river, the slope of the land (the speed of flow), the type of river bottom, and the turbulence or sluggishness of the stream.

The mineral matter found in most waters for industrial or home consumption consists of only a few salts in very dilute solution. It is a mixture of the bicarbonates, normal carbonates, chlorides and sulfates of sodium, calcium, and magnesium, with much smaller amounts of nitrates, iron, and aluminum. Even though these salts are few and in very small concentration they can cause a great deal of trouble, most of which is due to the hardness that they give to water. Both suspended matter and hardness are objectionable in water for textile uses. The problem of suspended matter can be solved by the selection of water which is free from it or by filtration or sedimentation in settling tanks. The question of hardness is not so easily answered.

HARDNESS IN WATER

Hardness in water is definitely associated with the soap-destroying power of the water; in fact, the soap-destroying quality of a water is a measure of its hardness. In most waters hardness is due to salts of calcium and magnesium and is confined to only the positive ions of these salts. Chloride, sulfate, carbonate, or bicarbonate ions do not make water hard, because they do not react with soap, nor does the sodium ion react with soap. But calcium and magnesium ions form insoluble compounds with soap. Recall that the general formula for a soap is RCOONa and that it reacts with calcium and magnesium ions as follows:

$$CaSO_4 + 2RCOONa \longrightarrow Na_2SO_4 + \underset{\text{(insoluble calcium soap)}}{(RCOO)_2Ca}$$

$$MgCl_2 + 2RCOONa \longrightarrow 2NaCl + \underset{\text{(insoluble magnesium soap)}}{(RCOO)_2Mg}$$

These calcium and magnesium soaps are fatty, greasy, insoluble solids, lighter than water, which form the well-known scum when soap is used with hard water. If a certain amount of soap is changed from a soluble compound to an insoluble one, then that amount of soap has been destroyed or at least changed to a form in which it has no cleaning power. These reactions and equations are of fundamental importance, and we shall refer to them many times in our study of textile chemistry. Any water that contains calcium or magnesium ions will precipitate an equivalent amount of soap. Not only does this waste soap and introduce a cost item, but the precipitated soaps cause much trouble.

There are many objections to hard water, some of them well known and others not so well known.

1. In laundering and cleaning, hard water wastes soap and other detergents and introduces an added labor cost, whether it is payroll labor or home labor.

2. Hard water leaves deposits on goods which are difficult to rinse off and which make the goods harsh and stiff. The life of textiles which are laundered frequently is shortened, and therefore there is an increased expenditure for wearing apparel and household linen. If large institutions had to launder with hard water, this would be a sizable expense item.

3. The scum resulting from the use of soap with hard water for toilet purposes is unpleasant: the ring left in the bathtub; the

deposit left on dishes; the well-known trouble found in washing hair with hard water.

4. Calcium salts will precipitate some dyes, and if hard water is used in the dye bath the goods will come up unlevel.

5. Sometimes goods that are washed in hard water before dyeing will come up with "lists," or darker streaks, because some calcium salts will have been left in the cloth and act as a mordant for the dye.

6. When hard water is used in a boiler or radiator a scale is deposited on the metal. This results in a loss in heat which means an added fuel cost and eventually the labor and material cost of removing the scale.

TYPES OF HARDNESS

There are two kinds of hardness in water, temporary hardness and permanent hardness. Temporary hardness is due to bicarbonates of calcium and magnesium and for the most part can be removed by boiling the water. The presence of such bicarbonates in hard water is due to the action of dissolved carbon dioxide in rain water on calcium carbonate in the soil. Rain water picks up carbon dioxide from the air and dissolves a small amount of it. When this solution comes into contact with limestone, $CaCO_3$, it converts some of the limestone into calcium bicarbonate, which is soluble in water:

$$CaCO_3 + CO_2 + H_2O = Ca(HCO_3)_2$$

In such a way is the temporary hardness of water formed. The result of boiling solutions of bicarbonates is shown by:

$$Ca(HCO_3)_2 + \text{heat} = CaCO_3 + CO_2 + H_2O$$

This shows that the soluble calcium bicarbonate is converted into insoluble $CaCO_3$ which precipitates and thus removes that much hardness. However, it is found that the boiling of water does not remove all the temporary hardness, unless boiling is continued for such a long time as to be impractical. After a reasonable amount of boiling there may be from 50 to 100 parts per million of hardness left in the water.

Permanent hardness in water is due to the presence of chlorides and sulfates of calcium and magnesium and cannot be removed by boiling. A small amount of permanent hardness is due to the normal carbonates of calcium or magnesium. We usually think of $CaCO_3$ and $MgCO_3$ as being insoluble in water, and yet they have a measurable solubility. A liter of water at room temperature will dissolve about 0.013 gm $CaCO_3$ and 0.1 gm $MgCO_3$. These are very small quantities, and waters which contain normal carbonates are usually saturated with these salts. The soluble sulfates or chlorides of calcium or magnesium or the difficultly soluble carbonates will react with soap to form insoluble soaps.

ALKALINITY OF HARD WATER

We must learn something about how bicarbonates and carbonates react with acids; that is, we must learn about the alkalinity of water. Three kinds of alkalinity may be found in hard water: hydroxide alkalinity, which is due to free OH ions; bicarbonate alkalinity, which is due to HCO_3 ions; and carbonate alkalinity, due to the normal carbonate ion, CO_3. Calcium hydroxide is soluble in water to the extent of about 2 gm/l but magnesium hydroxide is much less soluble, a saturated solution of it containing only about 0.01 gm/l. This would mean that a water high in magnesium could not contain very much hydroxide alkalinity. Both calcium and magnesium bicarbonates are easily soluble in water. However, their carbonates are quite difficult to dissolve ($CaCO_3$ = 0.013 gm/l, and $MgCO_3$ = 0.1 gm/l).

It is not possible for these three kinds of alkalinity to exist in the same water. Carbonates can exist along with either hydroxides or bicarbonates, but hydroxides and bicarbonates cannot exist in the same solution because they will react with each other:

$$NaOH + NaHCO_3 \longrightarrow Na_2CO_3 + HOH$$

Therefore, the alkalinity of water may be due to any one of the three or to mixtures of hydroxide and carbonate or of carbonate and bicarbonate. Usually it will be a mixture of carbonate and bicarbonate, and the bicarbonate will be present in the larger amount and will constitute the temporary hardness of the water.

Before going further we must discuss the conventions for expressing the characteristics of hard water. In the United States it is customary to express all types of alkalinity and all types of hardness in terms of parts per million of calcium carbonate (ppm $CaCO_3$). Parts per million is the same thing as milligrams per liter; e.g., if the total hardness of a water is 220 ppm $CaCO_3$, it is the same thing as saying that the hardness is equivalent to 220 mg or 0.220 gm $CaCO_3$ per liter. We do not talk about hydroxide alkalinity in terms of grams NaOH per liter because it might be $Ca(OH)_2$ or even KOH. We do not express the bicarbonate alkalinity in terms of $Ca(HCO_3)_2$ because it might be $NaHCO_3$ or $Mg(HCO_3)_2$, etc. But since equivalent weights of all alkalies are equal to each other (by definition), any type of alkalinity can be expressed in terms of any alkaline substance. That is, one equivalent weight of NaOH will require exactly the same amount of H_2SO_4 to titrate it as one equivalent weight of $CaCO_3$, or $Ca(HCO_3)_2$. And so any of the three kinds of alkalinity can be accurately designated in terms of $CaCO_3$. We might just as well express them as NaOH or $MgCO_3$ or CaO or Na_2O, but the convention in this country is to use $CaCO_3$, and the actual figures are parts per million of $CaCO_3$.

Temporary hardness, bicarbonate hardness, that hardness which can be destroyed by boiling, can be determined by titration. Let us see how the three kinds of alkalinity react with HCl:

$$NaOH + HCl \longrightarrow NaCl + HOH \tag{1}$$

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl \tag{2}$$

$$NaHCO_3 + HCl \longrightarrow NaCl + H_2CO_3 \tag{3}$$

How do the indicators show the end points of the reactions? Phenolphthalein is red with alkalies, and when the alkaline solution is titrated with an acid the end point occurs when the pink color disappears. However, at this point the solution might still contain alkalinity in the form of bicarbonate. That is, phenolphthalein will turn red in solutions of hydroxides and carbonates but not in bicarbonates. Thus the red color would disappear at the end of equation 2, at which time all the hydroxide alkalinity and half of the carbonate alkalinity will have been titrated. If methyl orange (yellow in alkaline solution and red in acid solutions) is then added, the other half of the carbonate alkalinity or an excess bicarbonate alkalinity can be titrated. In other words, at the end of the phenolphthalein titration the alkalinity left will be any original bicarbonate plus an amount of bicarbonate equivalent to one-half the original carbonate. Directions for making such titrations and the calculations involved are given in *Textile Chemistry in the Laboratory.*

DETERMINATION OF HARDNESS

The manner of expressing the hardness of water varies in different countries; that is, each country has a different scale of hardness, and these scales are expressed in the following ways:

The United States, in parts per million $CaCO_3$
Germany, in parts per 100,000 CaO
France and England, in parts per 100,000 $CaCO_3$

The British also still use the older Clark scale, in which 1° hardness is equal to 1 grain $CaCO_3$ per imperial gallon. It is obvious that the American scale of hardness is ten times as large as the French and English scales because we express it in parts per million instead of parts per 100,000.

Occasionally in this country we find hardness expressed in terms of grains per gallon, and one will frequently find it expressed in British journals in the same way. For these reasons we must understand the relations among several things so that we will be able to convert one system into another. We must know the relation between liters and gallons, grams and grains, and the British and American gallons.

1 ppm = 1 mg/l
1 ppm = 0.0584 grain per U.S. gal
1 ppm = 3.785 mg per U.S. gal
1 part per 100,000 = 10 ppm
1 gm = 15.432 grains
1 grain = 0.0648 gm
1 U.S. gal = 0.833 Brit. gal
1 Brit. gal = 1.2 U.S. gal
1 U.S. gal = 3.785 liters
1 Brit. gal = 4.542 liters
1 grain per U.S. gal = 17.12 ppm
1 grain per Brit. gal = 14.3 ppm

By means of these conversion factors, hardness of water may be changed from one system into another.

There are different ways for determining the hardness of water, some of which involve elaborate quantitative analysis, but, although that is the most accurate method, the simplest and most practical way is by means of soap titration. Since the hardness of water is equivalent to its soap-destroying power, all we need to do is to find out how much soap is destroyed by a certain volume of hard water.

A standard hard water is prepared, and an alcoholic soap solution is added to it in small portions, being shaken well after each addition, until a suds is formed that will stand up for 5 minutes. Then the soap solution is diluted so that each milliliter of it will be equivalent to 1 mg $CaCO_3$. If a 50-ml sample of hard water should require 5 ml of this soap solution to produce a 5-minute suds, the hardness of the water would be 100 ppm $CaCO_3$.

There is no sharp dividing line between soft and hard water, but as a general classification the following is offered:

Up to 50 ppm $CaCO_3$, the water is soft.
From 50 to 100 ppm, it is moderately soft.
From 100 to 150 ppm, it is slightly hard.
From 200 to 300 ppm, it is hard.
Above 300 ppm, it is very hard.

WATER SOFTENING

Water with hardness of 50 to 75 ppm $CaCO_3$ requires no softening for ordinary home or industrial purposes. Even with hardness as high as 125 ppm very little trouble is encountered, but when the hardness is above 150 ppm some means for softening is usually employed. Methods for softening water can be divided into three main types: (1) the lime-soda method, (2) the base-exchange method, and (3) the complete demineralization method.

The Lime-Soda Method

The lime-soda method for softening water is the oldest and is still most used for very large softening plants where personal control can be exercised. This method consists of treating raw hard water with calcium hydroxide (lime) and soda ash. We shall presently find that for most practical purposes soda ash need not be used because lime water alone accomplishes a satisfactory softening. In general we can say that the addition of lime removes temporary (bicarbonate) hardness and magnesium hardness, whereas the addition of soda removes permanent hardness. These reactions are shown by the following equations:

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow \overline{2CaCO_3} + 2HOH \qquad (4)$$

$$Mg(HCO_3)_2 + Ca(OH)_2 \longrightarrow \overline{MgCO_3} + \overline{CaCO_3} + 2HOH \qquad (5)$$

$$MgCO_3 + Ca(OH)_2 \longrightarrow \overline{\overline{Mg(OH)_2}} + \overline{\overline{CaCO_3}} \qquad (6)$$

$$MgCl_2 + Ca(OH)_2 \longrightarrow \overline{\overline{Mg(OH)_2}} + CaCl_2 \qquad (7)$$

Compounds with double lines above the formula are soluble with difficulty, but note that $MgCO_3$ is not so insoluble as $Mg(OH)_2$, and therefore in the presence of OH ions it will be changed to the much less soluble $Mg(OH)_2$, equation 6. Also note in equation 7 that, when permanent hardness due to magnesium salts is removed, an equivalent amount of calcium hardness is produced because $CaCl_2$ is soluble in water. The only hardness left is the permanent calcium hardness which can be removed by soda.

$$CaSO_4 + Na_2CO_3 \longrightarrow \overline{\overline{CaCO_3}} + Na_2SO_4$$

You now see what a small part soda plays in softening water, and why the softening is frequently done with lime alone. A typical example is a water with a total hardness of 245 ppm, of which 205 ppm is temporary and 40 ppm is permanent. This water was softened with lime, after which it was found to contain 25 ppm temporary and 40 ppm permanent hardness, a total of 65 ppm, which is soft enough for any ordinary purposes.

THE BASE-EXCHANGE METHOD

By base exchange we mean that hard water is passed through a siliceous material which will take out calcium and magnesium ions and replace them with sodium ions; that is, an exchange of bases occurs. The discovery that such a reaction could be brought about by means of certain hydrated silicates was made by Way in England in 1850, but nothing was done with it until 1906. At that time Gans prepared a synthetic hydrated silicate of sodium and aluminum which was called Permutit, and since that time the process has progressed to such an extent that several groups of materials are now available for large and small base-exchange softening plants.

The name zeolite is applied to these base-exchange softeners, of which there are two main groups, the siliceous and the carbonaceous. The former is the most used. The siliceous zeolites can be made synthetically from sodium silicate and sodium aluminate, or from such natural minerals as greensand. The carbonaceous zeolites will be mentioned when we discuss the demineralization of water. When water is passed through a substance like Permutit the following reactions take place, in which Permutit is represented by the formula Na_2P:

$$Ca^{++} + Na_2P \longrightarrow 2Na^{+} + CaP$$

$$Mg^{++} + Na_2P \longrightarrow 2Na^{+} + MgP$$

Calcium and magnesium ions in the water are replaced by sodium ions, and the Ca and Mg ions are combined with the acid part of the zeolite. After a time the zeolite has no more Na ions to exchange; that is, it becomes saturated with calcium and magnesium and can do no more softening. The feature that makes this method of softening water practical is that the exhausted zeolite can be rejuvenated or regenerated by passing a salt brine through it. This is another base-exchange reaction, in which the high concentration of Na ions in the brine replaces the Ca and Mg of the zeolite, and it is then ready to be used again.

$$2NaCl + CaP \longrightarrow Na_2P + CaCl_2$$

When hard water is treated with zeolites, the hardness is removed; that is, Ca and Mg ions are removed, and the soap-destroying power is neutralized, but the water still contains the same equivalent weight of mineral salts. It still has bicarbonates, sulfates, chlorides, etc., in it, but they are all sodium salts instead of calcium and magnesium salts.

DEMINERALIZATION OF WATER

By this method for softening water, not only are the hardness ions (Ca^{++} and Mg^{++}) removed, but all ions are removed, and the result is practically the same as distilled water. In fact many chemical laboratories are making their "distilled water" by this method.

Two steps and two entirely different reagents or absorbents are required for the complete demineralization of hard water. One reagent, the cation exchanger, replaces all positive ions with hydrogen ions; and the other reagent, the anion exchanger (better called the acid absorbent), takes out the acids formed in the first reaction. Both these reagents are organic and can be made from naturally occurring substances or synthesized by certain polymerization reactions. The use of synthetic resins as cation exchangers was discovered and patented in 1935 by Adams and

Holmes in England, and since 1937 the manufacture of such resins in this country has been licensed to the Resinous Products and Chemical Company. This resin is made by the polymerization of polyhydric phenols with formaldehyde and sold under the trademark Amberlite IR-1. The Permutit Company makes a cation exchanger by the sulfuration of coal and puts it on the market under the name Zeo-Karb H. Either of these reagents will replace the positive ions of hard water with hydrogen, leaving the water with an equivalent amount of acids, as shown by the following equations, where RH represents the cation exchanger, Zeo-Karb H or Amberlite IR-1.

$$Ca(HCO_3)_2 + 2RH \longrightarrow CaR_2 + 2H_2CO_3$$

$$CaSO_4 + 2RH \longrightarrow CaR_2 + H_2SO_4$$

$$MgCl_2 + 2RH \longrightarrow MgR_2 + 2HCl$$

$$NaCl + RH \longrightarrow NaR + HCl$$

Note that bicarbonates are changed to carbonic acid, which breaks up into CO_2 and H_2O, and the CO_2 can be blown out of the water. Note also that the only mineral acids left in the water are those of the permanent hardness of water and any sodium salts that might be dissolved in the water (except $NaHCO_3$). The first step in the dimineralization of water therefore is to pass the hard water through a column of Zeo-Karb H or Amberlite IR-1.

Reagents used in the second step, the removal of mineral acids, are synthetic resins made by the polymerization of amines, either aliphatic or aromatic, with formaldehyde. The Permutit Company calls its product De-Acidite, and Amberlite IR-4 is the resin sold by the Resinous Products and Chemical Company. When water that has been de-based (cations traded for hydrogen ions) is passed through the acid-absorbent mineral, acids are removed from the water and held on the absorbent. The only thing left in the water is some CO_2, which can be removed by passing the water through a degasifier unit. The reactions in the acid-absorbent unit may be represented by the following equations, where X represents the absorbent, e.g., De-Acidite or Amberlite IR-4.

$$H_2SO_4 + X \longrightarrow X{-}H_2SO_4$$

$$HCl + X \longrightarrow X{-}HCl$$

There is a limit to how much water can be demineralized by these two exchangers, just as there is a limit to how much water can be softened by Permutit before it must be regenerated. When the exchangers become exhausted they can be rejuvenated by flushing solutions through them. The cation exchanger is rejuvenated with a 3% HCl solution, or 1% H_2SO_4, and the anion exchanger is rejuvenated with Na_2CO_3 solution:

$$CaR_2 + 2HCl \longrightarrow 2RH + CaCl_2$$

$$X\text{—}H_2SO_4 + Na_2CO_3 \longrightarrow X + Na_2SO_4 + H_2CO_3$$

QUESTIONS

1. Why is well water harder than river water?
2. What kind of water (well, river, or rain) has the largest amount of suspended matter in it? Explain.
3. What are three main objections to the use of hard water for laundering?
4. Is the hardness of water caused by salts, acids, or bases? by negative or positive ions?
5. What are the two types of hardness in water? Give typical formulas for each, and show how they react with soap (equations).
6. Define temporary and permanent hardness.
7. How could you determine the hardness of water by a titration method, given a standard soap solution?
8. Write equations showing how temporary hardness (calcium) can be removed by the addition of lime. What chemical would be used to remove the permanent calcium hardness?
9. What is meant by the base-exchange method for softening water?
10. How are zeolites used in water softening?
11. Explain how a zeolite softener is rejuvenated.
12. What kind of a substance is Permutit?
13. What is meant by the demineralization of hard water? How is it accomplished?
14. What does a cation exchanger do?

5 · Classification and General Physical Properties of Textile Fibers

The textile fibers may be classified in several ways. For the purposes of a textbook the most reasonable divisions are natural and man-made fibers with subdivisions based on source of raw material. Therefore the following classification is submitted.

- I. The natural fibers.
  - A. Vegetable fibers.
    - 1. Seed fibers.
      - (*a*) Cotton. Grown in many countries. Three most important types are Egyptian, American, and East Indian. Used in all sorts of fabrics (Chapter 7).
      - (*b*) Kapok. From the inside of the seed capsules of a tree growing in tropical climate. Too smooth to spin but valuable for stuffing.
      - (*c*) Bombax wool. From seed covering of plants flourishing in tropical countries. Used for stuffing.
    - 2. Bast fibers.
      - (*a*) Linen. From flax grown mostly in Russia, Belgium, and Ireland. Used for a variety of fabrics.
      - (*b*) Hemp. Originally from Asia, growing in moist damp climate, it is now cultivated in Russia, Germany, France, Turkey, China, and other countries. Is quite resistant to weather and moisture, and so is used for ropes, sail and tent cloth, sacks, and bags.
      - (*c*) Jute. From a high tree-like plant growing in India, China, the East Indies. Used for carpet and linoleum backing, wall coverings, and sacks.
      - (*d*) Ramie. From India, China, Australia, and America. Strong, stiff, with silky luster. Used for sailcloth, ropes, upholstery fabrics, summer suitings, and paper.

      (*e*) Minor bast fibers such as Madras hemp, Bombay hemp, nettle fiber.
    3. Leaf fibers.
      (*a*) Sisal hemp. From Mexico and Central America. Used for making ropes, sailcloth, sacks, and carpets.
      (*b*) Manila hemp. From the Philippines, Java, and India. Used for making mats and ropes.
      (*c*) New Zealand flax. From New Zealand and India. Used for making ropes, twine, bags, and sailcloth.
  B. Animal fibers.
    1. Appendage fibers.
      (*a*) Wool. From sheep. World-wide production; Australia, New Zealand, British Isles, North and South America (Chapter 9).
      (*b*) Mohair. From the Angora goat in Asia Minor. For luster goods, plush, upholstery.
      (*c*) Cashmere. From Cashmere goat in the high mountain sections of central Asia. For fine worsteds, shawls, etc.
      (*d*) Alpaca, llama, and vicuña. From a small South American camel.
      (*e*) Camel's hair, rabbit fur, horsehair.
    2. Secretion fibers.
      (*a*) Mulberry silk. Natural silk. From silkworm in China, Japan, Persia, East Indies, Italy, and France (Chapter 10).
      (*b*) Wild silks. Tussah, eria, yamamai, and fogara. None is cultivated.
II. The man-made fibers.
  A. Fibers from vegetable sources.
    1. Cellulosic.
      (*a*) Viscose. Xanthate process (page 218).
      (*b*) Bemberg. Cuprammonium process (page 215).
      (*c*) Nitro. Chardonnet process (page 212).
      (*d*) Acetate. Acetylation process (page 228).
      (*e*) Rayolanda.
      (*f*) Carboxyethyl cellulose ether.
      (*g*) Ethyl cellulose.
      (*h*) Seaweed fiber (alginate).
    2. Protein.
      (*a*) Zein fiber (Vicara) (page 361).
      (*b*) Soybean fiber (page 369).
      (*c*) Peanut fiber.
  B. Fibers from animal sources.
    1. Casein fiber (page 360).

C. Truly synthetic fibers.
  1. High polyamide fibers. Nylon (page 307).
  2. Vinylite polymers. Vinyon (page 342).
  3. Vinylidene polymers. Saran (page 344).
  4. Acrylic fiber. Orlon (page 352).
  5. Polyethylene fibers. Polythene.

The word fibers is quite generally used in connection with these raw materials for textiles, and yet it is not precisely correct. These fibrous raw materials are divided into two classes, based on their length. It is correct to speak of wool or cotton fibers, but when speaking of silk, rayon, and nylon, the word "filament" is proper. Filaments are natural or manufactured fibers of continuous length. However, when rayon is cut into short lengths (for spinning with wool and cotton) it is known as staple rayon or staple fiber and is not considered a filament. Fibers for spun silk are also considered staple fibers.

Yarns are made from fibers by either carding or combing, and yarn may be given a large amount of twist in order to produce a firm solid yarn, or it may be given a small amount of twist which will yield a loose fluffy yarn. The arrangement of fibers in a carded yarn (carded cotton, or woolen yarns) is a scrambled one, with no definite plan, but in combed yarns (combed cotton, or worsted yarns) the fibers lie more or less parallel. Short fibers are not suitable for combing.

Long filaments, such as silk, rayon, and nylon, are twisted or thrown to make yarns, and, as with the spun yarns, a large or small amount of twist may be introduced. The amount of twist is governed by the specific uses for which the yarns are sold.

COUNT OF TEXTILE YARNS

The count of a yarn made from any fiber is a number which expresses the relation between length and weight. The weight factor is unconsciously associated with the size or fineness of yarn in the mind of the ordinary consumer. For example, one thinks of a #60 cotton yarn as being finer than a #40, but actually the two numbers are functions of the weights of the two yarns and not the cross-section dimensions of them.

There are two systems for expressing these length-weight relations: the count or number system, which is applied to all spun yarns; and the denier system, which is used for all continuous-filament yarns. These two systems are opposites, one being the converse of the other. In the count system a unit of weight is fixed, and in the denier system a unit of length is fixed.

The count of a spun yarn in the United States and Great Britain is the number of standard-length hanks or skeins in 1 lb. The length of the hank depends on what the fiber is; e.g., for cotton the length is 840 yd. If 10 such hanks are required to weigh 1 lb, the count of the yarn is 10; if 1 lb of cotton yarn contains 46 hanks of 840 yd each, its count is 46. The confusing thing about it is that if we are dealing with worsted yarns the standard length is 560 yd, and to complicate it still further woolen yarns are numbered on two systems, the cut system, in which the standard length is 300 yd, and the run system, in which it is 1600 yd. In the metric system the standard weight is 1 kg, and the length of the standard hank is 1000 m. In France the length is still 1000 m, but the standard weight is 500 gm. These standard figures will be found in Table 10.

TABLE 10

COUNT OF YARNS

STANDARD HANKS AND WEIGHTS

Standard Weight	Yarn or System	Standard Length
1 lb	Cotton, spun silk	840 yd
	Spun rayon	840 yd
	Woolen, cut system	300 yd
	Woolen, run system	1600 yd
	Worsted	560 yd
	Flax, hemp, jute	300 yd
1 kg	Metric system	1000 m
500 gm	French system	1000 m

The count of a yarn is determined by winding a definite number of turns of yarn onto a reel, the ordinary circumference of which is 1.5 yd. Sixty turns of yarn on such a reel would measure 90 yd. If 90 yd of a certain cotton yarn weighs 0.00357 lb, what is the count of the yarn? Such a weighing would not be made in terms of pounds, but of some smaller unit of weight, such as grams or grains. In most testing laboratories yarn is weighed in grains because the conversion of grains to pounds is simple (1 lb = 7000 grains). In the present example, 90 yd of cotton yarn weighs 25 grains. How shall we calculate the count? It can be done by substituting in the following equation:

$$C = \frac{L}{W} \times \frac{7000}{H}$$

where C = the count.
L = yards weighed.
W = weight in grains.
H = yards in standard hank.

The count of the yarn in our problem is

$$C = \frac{90}{25} \times \frac{7000}{840} = 30$$

Another example using worsted yarn: 120 yd weighs 50 grains; what is the count?

$$C = \frac{120}{50} \times \frac{7000}{560} = 30$$

The general equation by which these counts were calculated can be used for determining either C, L, or W for any yarn if two of them are known and if the standard hank length is known. That is, you can calculate how many pounds of 40's cotton you would have to buy in order to get 3,000,000 yd of it. It is customary to express these counts with the symbol ('s) following the number, together with a designation of the fiber or system. Thus the count in the first problem is 30's cotton, and in the second it is 30's worsted. Such numbers refer to single-ply yarns. When considering two- or three-ply yarns, the number of plies must be shown in the count. If two 60's single yarns are twisted together the result will be approximately size 30. This is not exactly true because some shrinkage occurs when two yarns are twisted, and the amount of shrinkage depends on how much twist is put in. It is customary to designate such ply yarns by using the count of the singles rather than the twisted yarn. The above yarn would be labeled 2/60's cotton, meaning that two 60's have been twisted together to make the yarn.

Perhaps the reader is impressed with the rather chaotic state of yarn numbering. There are too many systems and standards. In an effort to simplify the matter, the American Society for

Testing Materials has suggested a universal system called the typp system. The word typp is composed of the first letters of "thousand yards per pound." According to this system, the count of a yarn, regardless of what fibers it is made of, would be simply the number of thousands of yards of the yarn required to weigh 1 lb. Let us go back to the two yarns for which we calculated counts, both of which turned out to be 30's, and calculate the typp counts.

Ninety yards of the cotton yarn weighed 25 grains. All we need to calculate is how many thousands of yards of this yarn would weigh 7000 grains (1 lb).

$$90 : 25 = X : 7000$$

$$X = 25{,}200 \text{ yd in 1 lb}$$

$$\text{The typp} = 25.2$$

One hundred twenty yards of the worsted yarn weighed 50 grains. Therefore,

$$120 : 50 = X : 7000$$

$$X = 16{,}800 \text{ yd in 1 lb}$$

$$\text{The typp} = 16.8$$

To convert from the old count to the new typp count, multiply the standard hank length by the old count and divide by 1000.

The denier system for numbering yarns is based on the weight of a standard length of 9000 m (9842 yd) of a yarn, the weight being expressed in grams. Thus the denier of a filament or yarn is the weight (in grams) of 9000 m of the yarn. This is the same as the weight in grains of 638 yd of the yarn. Thus, if 9000 m of a silk yarn weighs 150 gm, it is a 150-denier (150-d) yarn; or if 638 yd of a rayon yarn weighs 75 grains, it is a 75-denier yarn. This is the system used for numbering silk, rayon, and nylon yarns, that is, all yarns made from continuous filaments. Spun silk and spun rayon yarns are designated by the count system. The denier of a yarn is a rough measure of its size. Recall that as wool or cotton yarns become heavier, the count or number of the yarn becomes smaller. That is, a #50 cotton yarn is heavier than a #80. With silk, rayon, and nylon, the opposite is true; i.e., the higher the denier, the heavier the yarn, so that an 80-denier rayon yarn is heavier than a 50-denier yarn.

It may be necessary at times to change from one system to the other, that is, to calculate the denier of a cotton yarn from its count or number. This can be done easily by means of the equation on page 101. The known count is substituted for C, the number 638 for L, and W becomes the unknown value (the denier), which will be the weight in grains of 638 yd of the yarn. The denier of a #60 cotton can be calculated as follows:

$$60 = \frac{638}{W} \times \frac{7000}{840} = 88 \text{ denier}$$

We have said that the denier of yarns is a rough measure of their relative size, but we must understand that this is only approximately correct. It is true that the lower-denier yarns are finer than those with higher deniers, but this relation is not one of exact direct proportionality. In other words, a 60-denier yarn is not twice as fine (or half as coarse) as a 120-denier yarn. The latter yarn weighs twice as much, but its diameter is not twice as great and hence its size is not twice as large. If one yarn is twice as heavy as another, its volume must be twice as great (assuming their densities are the same) but the radius will not be twice as great. However, the cross-section area will be twice as great, but this is proportional to the square of the radius and not to the simple radius or diameter. If we assume that the two yarns are perfect cylinders, the facts are that doubling the weight, or doubling the denier, will not double the radius but will increase it only about 43%.

The grex system for numbering yarns was tentatively proposed in 1945 by the American Society for Testing Materials, revised in 1946, and adopted by ASTM in 1947. It is a universal system applicable to any fibers, filaments, or yarns used in the textile industry. It is very much like the denier system, and the grex number of a yarn is almost the same as its denier, but the grex system is somewhat more logical because it is a direct decimalized system using metric units.

In the cgs (centimeter-gram-second) system, the unit of linear density is grams per centimeter, gm/cm. The grex unit is one-millionth of this. Therefore, the grex number (gx) of a yarn is the weight in grams of 10,000 m of yarn (10,936 yd). Note that the denier of a yarn is the weight in grams of 9000 m of yarn, and therefore the grex number is 1.1111 times as large as the denier.

It is seen that the grex of a yarn will increase with its weight per unit of length, and thus it is a measure of relative coarseness, or fineness, of various yarns made from the same fibers, or fibers of equal density. Density must be taken into consideration when using grex numbers for comparing fineness of yarns made from different kinds of fibers. For example, a 100-gx cotton yarn is not coarser than a 75-gx nylon yarn, because the density of cotton is 1.55, whereas the density of nylon is 1.14.

A number that is the weight in grams of 10,000 m of yarn is the same thing as the weight in grains of 708.6 yd of yarn. Thus the relation between the count of a yarn and its grex number is similar to that shown on page 102 except that the number 638 must be changed to 708.6.

The tenacity of fibers, filaments, and yarns can be expressed in terms of grex as well as in denier. For example, a tenacity of 4 gm/denier is the same as 3.6 gm/gx.

Properties of Textile Fibers

Of the natural fibers listed in the classification on page 97, only a few have been used over wide areas of the world by mankind for a period of many, many years. They are flax (linen), wool, cotton, hemp, and silk. Linen dates farther into antiquity than any of the other fibers. There are records of its cultivation and use in the Stone Age in Europe. The Swiss Lake Dwellers are known to have grown flax 4000 years before the Egyptians started cultivating it. The early Babylonians had a very highly developed textile industry in which flax, wool, and cotton were utilized. The early Greeks made wide use of wool. The Aztecs of Mexico and the Incas of Peru knew about cotton and hemp, and the use of cotton in India dates back to 1500 B.C. Silk was unknown to the early Europeans, but it had been used in China before history started in Europe.

Certainly over all these thousands of years men must have experimented with other natural fibers for textile purposes, and yet only five fibers have withstood the test and have continued to be used. True, other fibers have been employed for clothing in some parts of the world, but only because of the restrictions imposed by availability and transportation. As far as large-volume use is concerned, only five fibers have survived. We all know in what ways these fibers differ from each other, but there must be something more or less common among them to which can be attributed their survival. What did these five fibers have that the others did not have? If we can discover that, then we shall have what might be called the essential properties of fibers suitable for textile purposes.

As far as this book is concerned, the only interest is in fibers for making yarns that can be woven or knitted into fabrics, that is, goods which are generally used for clothing or household cloths such as tablecloths and draperies. We shall not be concerned with those fibers used for stuffing or packing or the makings of mats.

We can divide the properties of textile fibers into two groups: (*a*) the primary properties, which may be considered the essential properties responsible for the popularity of the five fibers for so many years; (*b*) the secondary properties, which are desirable, though not essential. There are five primary or essential properties: staple, strength, elasticity, uniformity, and spinning quality. These properties will be discussed in detail in the following sections.

STAPLE

The word staple is used in connection with the dimensions of a fiber, such as length and diameter, and we speak of a long- or a short-staple fiber, or a fine-staple fiber. When we say that staple is an essential requirement, we mean that a fiber must be long enough and fine enough to be satisfactory. A fiber might satisfy all the other requirements, but if it is not long enough it is not good enough. As we know, silk is a very long fiber, whereas cotton and wool are much shorter, but their spinning quality compensates for their short length.

The length of fibers varies greatly. For example, the length of cotton runs from 0.3 in. to about 2 in., fine wools from 1.5 to 5 in., and coarse wools from 5 to 12 in. Rayon and nylon manufacturers follow the system used by the silkworm and spin a filament that is almost endless. And yet, when rayon is to be spun with cotton or wool, it is cut into short lengths (staple rayon), about the same as the other fiber. Only one generalization can be made about length of fiber, and in making it we must confine ourselves to the same fiber. The longer the fiber, other things being equal, the stronger the yarn. That is, a long-staple sea island cotton will make a stronger yarn than ordinary upland cotton.

Similar remarks may be made about the fineness of staple of textile fibers. In general, the small-diameter fibers are the ones most prized. It is true that coarse fibers like jute and sisal can be spun into yarns and woven into cloth, but such cloths are coarse, rough, crude, and of low grade. On the other hand, fine filaments like silk and nylon can be converted into yarns and made into cloth which is prized for its fine, smooth, uniform, and draping quality. Fine fibers make fabrics that are more flexible and therefore drape better. Also they provide a larger fiber surface, which is an important factor in the heat-insulation capacity of fabrics.

TABLE 11

MEAN WIDTH OF FIBERS

Fiber	Mean Width, microns*
Acetate rayon	11–46
Cashmere	14–16
Cotton	16–20
Mohair	24–60
Nylon	18–24
Silk	9–11
Vinyon	16–18
Viscose	11–46
Wool	18–40

* 1 micron = 0.001 mm.
100 microns = 0.004 in.

To the untrained eye and touch almost all textile fibers are about the same size. It is easy to tell the difference between a 1-in. cotton fiber and a 1.7-in. fiber; but it is difficult to visualize the difference between a fine wool with a mean diameter of 0.00035 in. and a coarse wool with a diameter of 0.0018 in., and yet one of them is about six times as thick as the other one.

There is much variation in the width of fibers (the word diameter is not so good because very few fibers are round). Not only do various kinds of fibers have different widths, but there is a variation in width along the length of one individual fiber. There is a wider variation in the width of natural fibers than in the man-made fibers, because the process of manufacture of synthetic fibers produces fibers of more uniform width. For example, the width of silk and wool may vary from 18 to 30%, but the manufacture of nylon is so carefully controlled that the variation is usually not more than 5 or 6%. The diameter of silk filaments varies from 0.0004 in. to 0.0005 in., and in cotton the variation is from 0.00063 in. for American sea island to 0.00083 for some East Indian cottons. Even though we cannot appreciate the small differences in fineness of textile fibers we can get the impression that they must be very fine in order to be acceptable for making the types of cloth that we demand. Some high-polymer plastic fibers being manufactured have diameters of about 0.05 in. Even though this seems like a very small diameter, we can see that such a filament could not compete with silk or cotton. Table 11 shows the mean width of several common fibers.

STRENGTH

It is essential that a fiber be strong enough to be converted into yarns and then into fabrics that will be durable enough to satisfy the purpose for which they are intended. Some cloths must have great strength, whereas in others, such as those for decorative purposes, this quality is not so important. Part of the strength of a fabric is determined by the size of the yarns used in its construction, but no yarn can be stronger than the sum of the strengths of the individual fibers in the yarn, and thus we must consider the strength of the fibers themselves.

The strength of textile materials is expressed in various ways, depending on whether it refers to cloth, yarns, or fibers, or whether it means the kind of strength (bursting or longitudinal stretching strength). When the word strength is applied to fibers or yarns it is always used as a measure of the amount of tension required to break the fiber or yarn; applied to fabrics, it may mean the amount of tension required to break a strip 1 in. wide, or it may indicate the resistance of the cloth to a force that is like poking a hole in the cloth. This last is a test made on special-purpose fabrics and on all knitted fabrics. By the word strength we shall mean the resistance of fiber, yarn, or cloth to a longitudinal pulling force that breaks the material. With this meaning there are three methods for expressing strength. The strength of cloth is usually stated in terms of the pounds of force required to break a strip of the cloth 1 in. wide. The two terms applied to the breaking of a fiber or yarn are tenacity and tensile strength; they must be very carefully distinguished.

The terms *tenacity* and *tensile strength* describe the strength of filaments or yarns of any or all fibers on a common basis. The basis selected may be either area or weight. For example, it is customary to express tenacity in terms of grams per denier (gm/denier), that is, the weight required to break the yarn divided by the denier. If a filament is broken by a weight of 10 gm and the denier of the filament is 4, the grams per denier is 2.5, and this will be called the *tenacity* of the filament. This is a fair standard for all fibers because it puts the strength on a common basis, that is, the number of grams pull that would be required to break the yarn or filament if its weight were 1 denier. It is seen that tenacity, or grams per denier, is dependent on the density of the filament or yarn, a weight factor. On the other hand, *tensile strength* is usually expressed in terms of pounds per square inch (psi), that is, the number of pounds pull required to break the yarn if it were 1 sq in. in cross-section area. This puts it on a different common basis, and the strength of yarns of various fibers may be compared by calculating them to the common basis of a cross-section area of 1 sq in. With a little imagination it can be seen that two fibers of different densities might have the same tenacity but different tensile strengths. It is often necessary to change tenacity into tensile strength; that is, the grams per denier is known, but one wishes to express it in terms of pounds per square inch. Knowing the fundamental equation, denier = $900{,}000 \times A \times D$, and the values of A and D, such changes can be calculated.[1] To change tenacity, gm/denier, into tensile strength, psi, use

$$\text{psi} = \text{gm/denier} \times D \times (1.2791 \times 10^4)$$

To change psi to gm/denier use

$$\text{gm/denier} = \text{psi} \times \frac{7.812 \times 10^{-5}}{D}$$

We shall want to compare various fibers with respect to their strength or tenacity, and since textile fibers have different densities we must make some sort of calculation to put them on a common basis. Such a calculation is found in the following simple equation

$$\text{denier} = 900{,}000 \times A \times D$$

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[1] Sieminski, *Rayon Textile Monthly*, **24**, 585 (1943).

where A equals the cross-sectional area of the filament expressed in square centimeters, and D equals the density expressed in grams per cubic centimeter. This equation takes into consideration both weight and size.

TABLE 12

STRENGTH OF FIBERS

Fiber	Tenacity, gm/denier	Wet Strength a Percentage of Dry Strength
Acetate rayon (regular)	1.2-1.8	56–70
Acetate rayon (saponified)	4.8–6.5	65–88
Acetate rayon (high impact)	1.5	
Bemberg rayon	1.7–2.3	
Cotton (American upland)	3.0–4.9	110–130
Cotton (Egyptian)	4.2-5.5	110–130
Cotton (sea island)	4.4–6.3	110–130
Nylon (regular)	4.5-5.7	84–90
Nylon (high tenacity)	6.0–7.5	84–90
Orlon	4.0–4.8	90–93
Saran	4.0–6.0	100
Silk (raw)	4.0–4.6	
Silk (degummed)	2.8–4.9	75–95
Soybean fiber	0.6–0.8	30–35
Vinyon (regular)	2.0–2.8	100
Vinyon (high tenacity)	3.5–4.4	100
Viscose rayon (regular)	1.8–2.4	44–54
Viscose rayon (medium)	2.5–3.1	62–65
Viscose rayon (strong)	3.4–5.0	55–86
Wool	1.0–1.7	76–97

The strength of textile fibers is influenced by the moisture in the atmosphere where the strength test is made. In general, the natural vegetable fibers are stronger when they are wet, but other fibers are weaker when wet. Thus we must not compare the strength of cotton measured at a relative humidity (R.H.) of 85% with the strength of rayon measured at an R.H. of 30%. Whenever specific strength figures are given it is assumed that the determinations have been made at approximately 65% R.H. and ordinary temperature. Table 12 shows the relative strength of several fibers expressed in grams per denier. These values are taken from *The Man-Made Textile Fibers*, by Jules Labarthe, Mellon Institute of Industrial Research, 1945, and from other reliable sources.

Note how the fibers fall into five groups on the basis of how well they retain their strength when wet. Cotton is in a class by itself, being the only one that gains strength when it is wet. The vinylite and vinylidene resin fibers lose no strength when wet. Silk, wool, nylon, and Orlon fall into a group in which there is only a slight loss. All the rayons are considerably weaker in the wet state, and fibers like the casein and soybean fibers are extremely weak when wet, retaining only about one-third of their strength.

ELASTICITY

The third essential property for textile fibers is elasticity, included with which are such properties as elongation, elastic recovery, pliability, and bending strength. All these properties are interrelated so that the whole picture is rather complicated. Much of the quality of elasticity depends on the orientation (arrangement) of the molecules that make up the fiber and on the proportion of the fiber that has crystalline characteristics as contrasted with amorphous characteristics. If excessive orientation is produced by mechanical means the fiber loses much of its pliability and stretchability, but if the orientation is poor the fiber has less strength.

Fibers must be pliable enough to wrap around each other to produce a yarn, which in turn must be flexible enough to pass over and under other yarns when a cloth is woven. Many cloths must be able to resist repeated crushing or folding. Others must be able to withstand impacts; they must stretch enough to take care of such impacts and then spring back to their original shape or size, which means an elastic recovery. The elastic elongation of a fiber is definitely connected with its bending strength and its draping quality. In fact, most of the desirable features of smart clothing are dependent on this essential property of elasticity together with its associated properties.

All fibers can be stretched if enough tension is applied. This property of being stretchable is inherent in the individual fibers, and therefore among various fibers with their different chemical structures we should expect to have what might be called different stretchabilities. It is well known that wool is easily stretched, that silk is less so, and that ramie is stretched with difficulty. The stretching property of fibers is defined in terms of per cent elongation. If sufficient tension is applied to fibers they will stretch until they are broken. The percentage of increase in length at the time of rupture is known as the *elongation* of the fiber.

Elongation is another property inherent in the individual fibers, and in natural fibers it is restricted to a fairly small range. It can be changed very little except by tricks of plant and animal breeding. However, the elongation of man-made fibers can be modified considerably by variations in manufacturing techniques. If a manufacturing process is changed to increase the tenacity of a fiber, the elongation is decreased. The accepted theory of the physical structure of textile fibers and filaments is that long-chain molecules are oriented in a more or less orderly fashion and held together by intermolecular forces, which are responsible for the strength of the fibers. As a rule, the more perfect the alignment of molecular chains, the higher the tenacity and the lower the elongation (or the greater the brittleness). Among the naturally occurring substances, proteins and cellulose seem to be the only ones suitable for good fiber formation—hence the use of cellulose for rayon manufacture and the use of vegetable and animal proteins for making artificial fibers. However, it is found that certain high polymers of the amide type (nylon), vinylite type (Vinyon), vinylidene type (Saran), and acrylic type (Orlon) are also suitable. These are truly synthetic fibers, the manufacture of which has nothing to do with the modification of naturally produced long-chain molecules.

The per cent elongation of several fibers is shown in Table 13. These figures were determined at a relative humidity of 60%. They have been compiled from information given in the *Handbook of Plastics* by Simonds and Ellis, D. Van Nostrand Company, 1943, and in *Textile Fibers*, by Matthews and Mauersberger, John Wiley & Sons, 5th Edition, 1947.

One would think that a fiber could not be stretched unless it had some elasticity, and, therefore, that the per cent elongation should be a measure of elasticity. However, this would not be true because elasticity is not the property of being stretchable, but the property of being able to regain original length or shape after being stretched. It is not a question of how far a fiber can be stretched, but how much it will snap back afterwards. Actually, elasticity opposes elongation.

If any material is truly elastic it will obey the law of physics which says that the ratio of the tension (applied to such material) to the strain produced by such a tension is a constant. This constant is known as Young's *modulus of elasticity*. It can be reduced to a common basis of either strain or tension. For example, the tension required to stretch various fibers 1% would be the modulus for each fiber. Or, conversely, one might apply the same tension to various fibers and measure the variation in the amount of elongation. It is customary to express the modulus in two ways: (*a*) as pounds per square inch cross-section required to stretch a fiber 1%, or (*b*) as grams per denier required to elongate 1%. If some fibers are more easily stretched than others, less tension will

TABLE 13

ELONGATION OF FIBERS

(Percentage of increase in length at the break)

Fiber	Dry Elongation	Wet Elongation
Acetate rayon (regular)	23–30	30–38
Acetate rayon (saponified)	6.0–6.5	
Acetate rayon (high impact)	50	
Bemberg rayon	15–20	27–35
Cotton	3–7	
Hemp	3–5	
Nylon (regular)	18–22	17–30
Nylon (high tenacity)	13–16	12–30
Orlon	16–21	15–20
Ramie	3–6	
Saran	20–30	
Silk (degummed)	13–20	
Silk (Bombyx outer filaments)	10	
Silk (Bombyx inner filaments)	15	
Silk (Antheraea outer filaments)	16	
Silk (Antheraea inner filaments)	25	
Soybean fiber	40	
Vinyon (regular)	14–35	30–35
Vinyon (strong)	18–20	16
Viscose (regular)	16–20	18–35
Viscose (medium)	16–20	20–27
Viscose (strong)	9–19	14–22
Wool	20–35	

be required to stretch them 1%, and consequently their moduli of elasticity will be smaller. Hence, the modulus of elasticity is inversely proportional to the elastic properties of fibers. Since most fibers will stretch more easily when wet, and hence exhibit a smaller modulus, it is necessary that the relative humidity of the atmosphere in which the determination is made be stated. A du Pont bulletin (1943)[2] gives the results of tests made in their laboratories. These tests were performed at 72% R.H., and the results were calculated to a basis of grams per denier. The figures are shown in Table 14.

TABLE 14

TENSION REQUIRED TO STRETCH FIBERS 1%

Acetate rayon	0.4 gm/denier
Cotton	0.5
Nylon (unshrunk)	0.25
Nylon (shrunk)	0.1–0.15
Orlon (1.5% stretch)	0.8
Ramie	0.9
Silk	0.75–1.16
Viscose	0.7
Wool	0.32

It has been pointed out that the elasticity of a fiber is its ability to recover or snap back to its original length after having been stretched. This is known as elastic recovery and is expressed in percentage. That is, if a fiber or yarn is stretched a certain amount by applying some load to it, and then the load is removed, the fiber or yarn is said to have an elastic recovery of 100% if it goes back to its original length. If it shrinks only 0.6 of its extra length (as the result of stretching), its elastic recovery is 60%. Elastic recovery is an effort to oppose dimensional distortion. That is, if the shape or size of a material is altered by pulling or stretching, the material will try to overcome such an effect and regain its original size and shape. If its dimensions are temporarily distorted, it will attempt to regain them. This may take place slowly over a period of time, or it may occur rapidly. Rubber is a material that recovers very rapidly after stretching, snapping back to its original length or shape; but most of the textile fibers recover much more slowly.

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[2] *The Physical-Chemical Properties and Processing of Nylon Textiles.*

This recovery is similar to the action of a coil spring. When a pulling force is applied to it, a spring can be extended or stretched and held in such an elongated state, but as soon as it is released it will return to its original contracted form. Some metals make good springs and others do not. So it is with fibers. Some of them have a good ability to recover and others do not. This individuality among fibers must have some connection with their internal chemical structure. The modern ideas regarding the structure of wool (see page 260) are based on the fact that wool can be stretched, and unless it is set in this stretched form it will return to its original length when released from the distorting force. The property of elastic recovery is the opposite of setting. In setting, a fiber or fabric is distorted, and while in such a condition may be treated so that it will retain its new form, but if such a treatment is not applied the fabric will not retain the new form but will seek to recover its old form. Thus we find that elastic recovery is inherent in each type of fiber. and that its force or extent is different for each type. The animal and protein-like fibers seem to have the best recovery. This may be because nature orients and disposes the constituent molecules in the proper way so that intermolecular recovering forces can be operative. In the field of synthetic fibers it is left to man's ingenuity to imitate nature.

Elastic recovery of fibers is a very important property, and it is essential that fibers and fabrics have a good recovery if they are to maintain their shape and to fit enclosed contours properly. Much of our wearing apparel is constantly being subjected to stretch and strain, and it is highly desirable that it repeatedly recover from such distortion. Fabrics or knit goods made from fibers with good elastic recovery will do so, but if they do not have good recovery the well-known bagginess will result. The superior clinging property of silk and nylon is due to their high elastic recovery.

Four factors affect the extent of elastic recovery, and if the measurement is to have any value, especially when used to compare two or more materials, these factors must be understood and rigidly controlled when the experimental determination of recovery is carried out. The factors are as follows. The first is the amount or extent of stretch. If fibers are stretched too much, that is too far, they will be so internally disorganized and strained that their normal recovery ability is decreased. Each type of fiber has a limiting elongation beyond which its ability to recover is sharply changed. This elongation is known as the true elasticity of the fiber or the elastic limit and is expressed in percentage. It designates the maximum percentage that a filament or yarn can be stretched and still have an elastic recovery of 100%. For example, nylon can be stretched about 8% and still recover completely after the stretching load is removed, but if it is stretched more than 8% it will not recover completely.

TABLE 15

ELASTIC RECOVERY

Fiber	Percentage of Stretch	Percentage of Recovery after Amount of Stretch Shown in Column 2
Acetate rayon	4	50–65
	14	29
Nylon	4	100
	8	100
	16	91
Orlon	2	100
	4	95
Saran		Fair; slow
Silk (raw)	4	50
Silk (degummed)	4	76
	8	56
	16	47
Vicara	2	100
	5	97
Viscose	4	50–65
	14	29

The time during which the material is held in its stretched form is the second factor. It is reasonable to imagine that, if this time is too long, some of the strained bonds in the material may be ruptured and cause the molecules to rearrange themselves in such a way as to change the power of recovery.

The third factor is another one involving time; it is the time interval between the release of tension and the measurement of the recovered length. Some of the fibers may recover more slowly than others and exhibit what is called delayed recovery.

The fourth factor involves the conditions under which the recovery is allowed to proceed. There are two ways in which this is done in the testing laboratory: (1) by allowing the fiber to recover without any opposing force (against no load), or (2) by giving it a load of some sort to support while it is recovering (against a load).

Table 15 shows the elastic recovery of a few fibers after the given amount of elongation.

More should be said about delayed recovery. If a stretching load is applied to a fiber or yarn smaller than the load required to break it, it is found that there is an immediate and rapid elongation followed by a much slower extension of the material. The rapid elongation is due to the true elastic property of the fibers, but the slower extension is probably due to plastic properties. Now observe what happens when the stretching load is removed. There is an immediate and rapid shrinkage which is approximately equal to the rapid elongation observed when the load was first applied. Then a much slower contraction occurs; in fact, it is so slow that the word creep is applied to it. The yarn or fiber will continue to creep until it has recovered practically all its original length. This property of creep is very important for many reasons. If too much tension is put on yarns during winding or warping or weaving, the slow shrinkage may be very undesirable. Creep is probably due to the plasticity of the fiber rather than true elasticity, and, since plastic flow is enhanced by moisture, excessive shrinkage of certain fabrics may be expected during humid weather.

Uniformity of Staple

Uniformity of staple is the fourth essential property of textile fibers. It is true that a woolen cloth can be made from fibers that vary in length and diameter, but such a cloth would not be acceptable to the discriminating consumer. If fibers have the same dimensions they will spin better and make a much more uniform and smoother yarn. This is one reason for sorting wool fleeces and separating the fibers into various qualities. For the some reason wool fibers are combed so as to yield a more uniform staple for spinning.

Spinning Quality

The fifth essential property is spinning quality, which means that the individual fibers must be capable of being spun into a yarn that will have sufficient strength to withstand loom punishment and to make a cloth that is strong enough. In order to have good spinning quality, fibers must have some cohesiveness; that is, they must be able to cling together in a mass and therefore stick together when spun. This prevents fiber slippage along the length of a yarn.

The only way in which the property of cohesiveness can be made operative is by having intimate points of contact between fibers, and thus, the greater the number of such points in a yarn, the less slippage there will be and the stronger the yarn will be. Microscopic examination of spun yarns shows that there is not much contact between fibers along the length of the fiber but that it occurs at isolated points.

Four main factors contribute to cohesiveness between fibers in a yarn: fineness of staple, nature of surface, pressure, and length. A mass of fine fibers will have a much greater total surface area than coarse fibers, and therefore the chances for contact are greater. The nature of the fiber surface is a very important factor in spinning quality because it may increase fiber-to-fiber contact. The serrated surface of wool, the spiral twist in cotton, the striations in certain staple rayons, and the rough knotlike surface of linen are examples of fibers with splended spinning quality. If fibers are pressed closely together we should expect more cohesiveness. This pressure is obtained by putting sufficient twist into a yarn. When long fibers are twisted together there are many more opportunities for fiber contact, which contributes to the general strength of the yarn.

Many other fiber properties are desirable or play a definite part in the formation of fabrics for special purposes. Among desirable but not necessarily essential properties we might mention density, or specific gravity; luster; moisture regain; flammability; felting quality; resistance to heat, etc.

DENSITY OR SPECIFIC GRAVITY

The relative weights of textile fibers are expressed in terms of density or specific gravity. Density is usually expressed as grams per cubic centimeter, whereas the specific gravity of a solid or liquid is a ratio of the mass of the substance to the mass of an equal volume of water (at 4° C). For all practical purposes the weight per cubic centimeter is the same as specific gravity.

The density of fibers is, of course, the determining factor in the weight of cloths that may be made from them. The heavier

TABLE 16

DENSITY OF TEXTILE FIBERS

Acetate rayon	1.30–1.33 gm/cu cm
Aralac	1.29
Bemberg rayon	1.52–1.54
Cotton	1.48–1.54
Fortisan	1.52
Hemp	1.48–1.50
Jute	1.48–1.50
Linen	1.50
Mohair	1.30–1.32
Nylon	1.14
Orlon	1.18
Ramie	1.51
Saran	1.70–1.72
Silk (raw)	1.30–1.37
Silk (degummed)	1.22–1.25
Silk (tussah)	1.27
Vicara	1.25
Vinyon	1.33–1.35
Vinyon N	1.29–1.30
Viscose rayon	1.52–1.54
Wool	1.30–1.32

fibers might be assumed to be the strongest, but there are many applications for which a strong, but lightweight, fabric is required. For such purposes the ideal fiber is one with a low density but high tenacity.

Density figures may serve for a rough determination of the percentage composition of a yarn composed of two different fibers by means of the formula

$$\frac{X}{100 - X} = \frac{d - d_2}{d_1 - d}$$

where X is the percentage of fiber 1.
d is the density of the mixture.
d_1 is the density of fiber 1.
d_2 is the density of fiber 2.

Table 16 shows the densities of a number of textile fibers.

MOISTURE ABSORPTION BY TEXTILE FIBERS

Most fibers will absorb moisture from the air, but the amount of moisture varies with the kind of fiber, its condition (loose, in yarn, or in cloth), and the humidity of the atmosphere. Outstanding exceptions to this are Saran and Vinyon, which absorb practically no water at all. Fibers have the property of taking on water and also of losing water, and the humidity of the air determines which of these phenomena will take place. If a dry cloth is placed in a damp atmosphere it will take on water, but if a damp cloth is placed in dry air it will lose water. These reactions will proceed until a condition of equilibrium is established, and the amount of moisture in the textile material will remain constant as long as its environment retains a constant humidity.

The absorption and retention of water must be considered from two points of view, based on the ease of absorption as contrasted with the ability to retain water at the point of moisture equilibrium. For example, cellulosic materials, such as blotting paper, filter paper, and cotton or linen dish towels, will absorb large amounts of water quickly, whereas wool will not. However, the condition of dish towels after such rapid absorption is not an equilibrium condition, and most of the water will be given up to the air until equilibrium is established, at which time it will be found that wool has retained more than twice as much water as cotton. A discussion of the moisture relations of textile fibers is usually confined to water retention, and any figures quoted refer to moisture equilibrium conditions.

There are two methods for expressing the amount of water in a textile material, in both of which it is a percentage, but the percentages are based on two different things. We have learned that percentage is the part divided by the whole. The part in this instance is a weight of water in a cloth or loose fiber, but the whole can be taken in two different ways. For example, suppose a 5-gm sample of raw wool is analyzed and found to contain 0.5 gm water, which is the part. If the whole is 5 gm, which is the weight of air-dry wool, then $(0.5 \div 5) \times 100 = 10\%$ moisture in the wool. When calculated in this way, it is known as the per cent moisture, or the per cent moisture on an air-dry basis. However, the 0.5 gm of water in the sample may be considered in an imaginary way as having been regained or taken up by a certain amount of bone-dry or oven-dry wool. The 5-gm sample of wool contains 0.5 gm water and 4.5 gm bone-dry fiber. The 4.5 gm bone-dry wool may be considered to have gained 0.5 gm water, and the percentage gained would be $(0.5 \div 4.5) \times 100$, which is

11.11%. This is known as the per cent *moisture regain* (usually called regain). Here the percentage is based on bone-dry wool instead of air-dry wool. It is better to think in terms of regain rather than moisture, because regain will be constant. If the 5-gm sample of wool were transferred to an atmosphere where the relative humidity is higher, it would absorb more water and weigh more than 5 gm, and its per cent moisture would be different, but the weight of bone-dry wool in it would remain the same.

TABLE 17

STANDARD REGAINS AND MOISTURE CONTENT

(65% R.H. and 70° F)

Material	Percentage of Regain	Percentage of Moisture
Acetate rayon	6.	5.56
Cotton yarn	7.	6.54
Cotton, mercerized	8.5	7.83
Flax and hemp	12.	10.71
Jute	13.75	12.09
Nylon	4.2	3.78
Orlon	1.0	1.0
Saran	0	0
Silk	11.	9.91
Vicara	13.	11.5
Vinyon	0	0
Viscose rayon	11.	9.91
Wool	16.	13.79
Wool noils	14.	12.28
Wool tops, oil-combed	19.	15.97
Wool tops, without oil	18.25	15.43
Woolen yarn, carded	17.	14.53
Worsted yarn	14.	12.28

Manufacturers, buyers, and sellers of textile materials have set up certain standards for commercial purposes. The American Society for Testing Materials has established such a set of standards, shown in Table 17. The figures in the second column are the standard regains for the materials listed; they approximate the per cent of water that each material would absorb if exposed to an average or normal atmosphere, which is assumed to have a relative humidity of 65% at a temperature of 70° F. The third column in the table shows the per cent moisture (not regain) under these conditions. This table shows that wool has the highest regain and the synthetic fibers the lowest, and that other natural fibers are intermediate.

It has been pointed out that a change of environment brings about a different moisture content. Table 18 shows the per cent moisture in textile fibers when they are at equilibrium in atmospheres of different relative humidity. These figures were determined at a constant temperature of 75° F.

Changes in moisture content of textile materials have a profound effect on the practical uses of such materials. For example, all the ordinary fibers except cotton have a lower tensile strength when they are wet. This decrease in strength is not a sudden phenomenon but becomes apparent as the humidity of the air increases. Not only do fibers lose strength when they are wet, but also they stretch more easily. This is important because, during winding, warping, and weaving operations, excessive tensions may be applied. When this tension is released the material will recover part of the extra length at once, but further shrinkage, due to creep, is sure to occur. The water-absorbing property of fibers is closely connected with heat insulation or heat transfer. Cotton is used so extensively in the tropics because of its large capacity for absorbing moisture, which evaporates and causes a lowering of temperature. If cotton cloth is treated to make it water-repellent, it will not absorb water and hence will be uncomfortable to wear next to the skin in hot weather.

TABLE 18*

PERCENTAGE OF MOISTURE AT DIFFERENT RELATIVE HUMIDITIES

(Temperature = 75° F)

Relative Humidity	Silk	Cotton	Wool	Nylon
20	5.4	3.6	7.1	1.4
40	7.8	5.0	11.0	2.3
50	8.8	5.7	12.6	2.8
60	9.9	6.7	14.2	3.4
80	14.0	9.9	18.6	5.0
90	18.4	13.6	23.2	5.7

* Matthews and Mauersberger, *Textile Fibers*, John Wiley & Sons, 5th Edition, 1947.

One fiber property that is important in the use and maintenance

TABLE 19

RESISTANCE TO HEAT

Fibers	° C at Which Loss in Weight Begins	Melting Point, ° C
Acetate rayon	95–105	200–230
Cotton	150	....
Nylon	225	250
Saran	75	115–140
Silk	150	....
Vicara	150	250
Vinyon	65	130
Viscose	150	....
Wool	135	....

of fabrics is resistance to heat. Some fibers lose considerable strength when subjected to a little too much heat. This, of course, must be taken into consideration when ironing fabrics. Table 19 shows the temperatures at which a measurable loss in strength may be expected. The melting points of a few fibers are also given.

QUESTIONS

1. Name some vegetable fibers that are seed fibers, some that are bast, and some that are leaf fibers.
2. Name some animal fibers that are like hair.
3. Name six man-made textile fibers.
4. What is the difference between fibers and filaments? What is the difference in the ways in which they are converted into yarns?
5. What is the principle on which the count system for numbering yarns is based? the denier system? the typp system?
6. What is the count of a cotton yarn 120 yd of which weighs 40 grains?
7. What are the five essential properties of textile fibers?
8. State the meaning of the following terms: staple, tenacity, tensile strength, elasticity, elastic recovery, elongation, creep, spinning quality, density, and regain.
9. Compare (as to whether greater or less) the wet and dry strength of cotton, linen, wool, nylon, and rayon.
10. What is the denier of a rayon yarn 70 yd of which weighs 10 grains?
11. How does per cent elongation usually vary with the moisture content of the air (relative humidity)?
12. Compare the elastic recovery of nylon, rayon, and silk.
13. Explain why some fabrics creep (shrink slowly).
14. What physical factors give a suitable spinning quality to cotton, silk, wool, and nylon?

15. What factors contribute to the cohesiveness of fibers in a yarn?

16. Give examples of very heavy, very lightweight, and intermediate-weight fibers.

17. If a dry cloth is moved from an atmosphere of 40% R.H. to one of 75% R.H., what will happen, and for how long?

18. What is the difference between the per cent moisture in a batch of raw wool and the regain of raw wool?

19. Compare the following fibers with respect to their moisture-absorbing capacity: cotton, nylon, wool, vinylite, rayon, and silk.

6 · The Chemistry of Cellulose

Cellulose is one of the main constituents of all plants, grasses, and trees, but only in the cotton fiber is it found in a fairly pure uncombined form. That is, cotton cellulose can be freed from most of its impurities by mechanical or solvent action, whereas other sources require chemical action. In plants like flax and hemp, the cellulose is combined with noncellulose constituents to form what are known as compound celluloses. Of these there are two main types: (*a*) the lignocelluloses, in which cellulose is combined with lignin (flax, hemp, jute, wood; and the lignified tissues of perennial plants), and (*b*) the pectocelluloses, in which the noncellulosic constituents are related to pectic acid (ramie, hemp, and flax). Cotton contains about 91% cellulose; and hemp, ramie, and flax contain similarly large amounts of cellulose. Wood and cereal straws contain lower proportions of cellulose—about 60% for coniferous woods and 30 to 40% for straws. In this book the word cellulose will be assumed to mean cotton cellulose, and the words cellulose and cotton will be used interchangeably many times. If we can learn a few facts about the chemistry of cellulose, then we shall have learned many of the fundamentals of the chemistry of cotton.

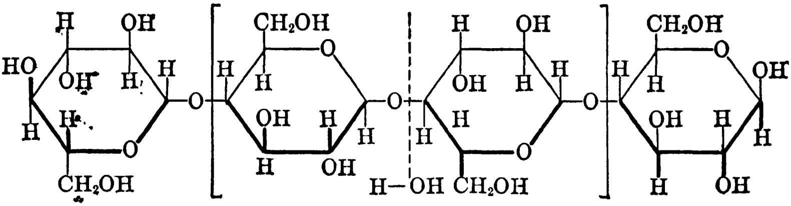
The brief study of cellulose in this chapter has been organized in the following way:

1. The structure of cellulose, with emphasis on its use in textile chemistry and technology.
2. The viscosity of cuprammonium solutions of cellulose and its reducing property. These two properties are widely used in studying the degrading effect of many reagents on cellulose.
3. The dispersion of cellulose in liquids.

4. Chemical reactions that degrade cellulose and change both its physical and chemical properties.

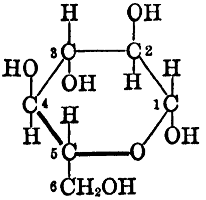
5. Chemical reactions that are not primarily degradation reactions.

After a hundred years of research on the behavior of cellulose, it has been accepted that it is a high-polymeric long-chain compound, the repeated unit of which is anhydro-β-cellobiose, these units being joined together by glycosidic linkages and each cellobiose unit being composed of two anhydroglucose pyranose rings. The structural formula is shown here.

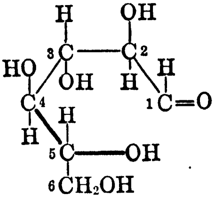


The portion of the formula for cellulose enclosed in brackets is the anhydrocellobiose unit. If this unit is split as shown by the dotted line, it will yield two fragments of anhydroglucose. Glucose is a simple sugar with the molecular formula $C_6H_{12}O_6$. Anhydroglucose would be this formula minus water, or $C_6H_{10}O_5$.

Glucose is an equilibrium mixture of two structures, the pyranose ring structure and the aldehyde form. These are shown below:



The Pyranose Ring Form



The Aldehyde Form

Note how the carbons are numbered. This is important because these rings are found in cellulose, and we shall use this same system for numbering them. The aldehyde form of glucose is the one responsible for the fact that glucose is a reducing sugar and will reduce Fehling's solution. Note that the aldehyde structure is formed from the pyranose ring by the migration of a hydrogen atom from carbon 1 to the oxygen of the ring, thus opening the ring and leaving carbon 1 in an aldehyde group. It is important to remember that any glucose ring structure in which there is a secondary alcohol group in position 1 is a potential reducing agent, because of the possibility of opening the ring with the formation of an aldehyde group.

Now look at the structural formula for cellulose on page 125. The long chain is made of repeated cellobiose units (in brackets), together with two terminal rings. Note that the terminal ring at the left end cannot open up to form an aldehyde group (because carbon 1 is not a CHOH group), but the terminal ring at the right end can form an aldehyde group. Thus cellulose has one potential reducing group at one end of each very long chain, but this one reducing group is such a small proportion of the total chain that pure cellulose does not show any reducing property (within the limits of the sensitivity of the methods used for such determinations). Let us condense the formula for cellulose. If we disregard the spatial arrangement of the molecule, and if anhydrocellobiose is equal to two anhydroglucose fragments, we may say that the cellulose molecule is a long chain of repeated anhydroglucose units with two terminal groups, and a condensed formula would then be

$$C_6H_{11}O_6—(C_6H_{10}O_5)_n—C_6H_{11}O_5$$

A still further condensation can be made if we forget the two terminal groups and say that cellulose is $(C_6H_{10}O_5)_n$, or that it is a high-polymeric chain of anhydroglucose units. We shall therefore write the molecular formula for cellulose $(C_6H_{10}O_5)_n$.

The structural formula for cellulose on page 125 shows a solid figure existing in space. The members of the rings lie in one plane with H and OH groups above and below it. The use of heavy and thin lines emphasizes this, because the heavy lines represent valence bonds which can be seen when the model is held level with the eyes. Note that the CH_2OH group and the O which joins the rings are always on the same side of the plane of the ring, either above or below it.

The chemist is not so much interested in spatial arrangements as he is in functional groups and cleavage products. It is seen that the functional groups in cellulose are all alcohol groups, three in each glucose unit, one primary and two secondary. These are the points at which cellulose is oxidizable (bleaching of cotton is an oxidation reaction). As far as cleavage is concerned, it is accomplished by acid hydrolysis, with the result that the cellulose chain is split into shorter chains, at one end of which a new reducing group will be formed.

By "splitting the chains" we mean the rupture of glycosidic linkages. The vertical dotted line in the formula on page 125 illustrates such a point of cleavage. If the chain is hydrolyzed at this point so as to put an H on the left side of the line and an OH on the right side, thus breaking the chain, the result will be the formation of two new terminal groups. We now have two chains instead of one. The new terminal group of the left chain has a CHOH group in the 1 position, and we have just learned that this is the potential aldehyde group of glucose. The new terminal group of the right chain has a new OH group, but it is not in the 1 position and so has no reducing possibilities. However, the other terminal of the right chain is still a reducing group. Thus we see that the result of one hydrolytic cleavage of a long cellulose chain is the formation of an additional reducing group. If we multiply this by several hundred, we can see that hydrolyzed cellulose should be a fairly good reducing agent. If we extend it still further and let the splitting continue, we can see that the final product will be glucose. It is found that a practically 100% yield of glucose can be obtained by the acid hydrolysis of cellulose.

The present-day idea of a model for native cellulose is one of long parallel chains of anhydroglucose units arranged in bundles called micelles. The strength of cellulosic fibers is dependent on the forces existing within these bundles. It is evident that along the length of the chains the cellobiose and anhydroglucose units are bound together by primary (ordinary) valences that are as strong as steel. The separate chains are held together laterally by secondary valences connecting oxygen atoms in adjacent chains, or by hydrogen bonds. There are other ways in which cross-links between chains may be formed. Heuser[1] shows that such links might be produced by a condensation of OH groups of adjacent chains (with the elimination of water to yield an ether linkage), or by a glycosidic linkage between the fourth OH of a terminal group with the reducing end group of an adjacent chain, or by the introduction of new atoms between adjacent chains.

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[1] *Paper Trade J.*, **122** (TAPP), 21 (Jan. 1946).

Man-made cross-links can be formed in various ways. For example, nitrocellulose can be dissolved and treated with lime to form a product with much different properties. It is presumed that this new material has calcium atoms between some of the adjacent chains. Methylene groups, CH_2, can also be introduced between chains by means of formaldehyde, CH_2O. Such cellulose-formaldehyde derivatives can be made with greatly different properties. Some of them resist the action of alkali and swell much less with NaOH, and have a reduced solubility in Schweitzer's reagent. On the other hand, U.S. Patent 2,397,437 (1946) treats alkali cellulose with formaldehyde to yield a fibrous product that is much more soluble in dilute NaOH.

The secondary valence forces are effective within the micelles, and then the micelles themselves are held together by tertiary forces known as van der Waals' forces, and when a fiber breaks it is due to the rupture of these forces, permitting the micelles to slip past each other.

For further reading on this subject, the following outstanding papers may be consulted:

Meyer and Mark, *Ber.*, **61**, 593–614 (1928).
Sponsler and Dore, *Ann. Rev. Biochem.*, **5**, 62–80 (1936).
Clark, *Ind. Eng. Chem.*, **22**, 474–487 (1930).
Astbury, *J. Textile Inst.*, **23**, T17–34 (1932); **27**, P282–297 (1936).
Davidson, *J. Textile Inst.*, **27**, P144–168 (1936).
Heuser, *The Chemistry of Cellulose*, John Wiley & Sons, 1944.

The textile chemist must be able to deal with problems connected with all sorts of processes and operations through which textile materials must pass during preparation for consumer use. He must develop methods for following the course of any fiber degradation that may accompany certain treatments given the material; he should be able to set certain limits above which or below which, as the case may be, damage may occur. If he is dealing with cellulosic fibers (cotton, linen, rayon) he has two important tools that he may use. These are the measurement of the viscosity of solutions of cellulose in cuprammonium hydroxide, and determination of the reducing power of cellulose in terms of copper number.

Cellulose and its derivatives, along with some other high-polymer substances, has the distinction of increasing the viscosity of cuprammonium hydroxide to a large extent, even in solutions as dilute as 0.5%. This high viscosity is directly connected with the length of the chains in the polymer. That is, if cellulose is degraded by any chain-shortening treatment, the viscosity of its solution will be lower and it will flow more rapidly.

There are three ways in which the flow quality of a liquid or solution can be expressed. The time of flow of a definite volume of liquid can be compared with some standard liquid. For example, Clibbens and Geake[2] (in a very fine comprehensive discussion of the technique of viscosity determinations and their significance) compare the time of flow of 0.5% cuprammonium solutions of cotton with a mixture of glycerin and water having a specific gravity of 1.1681. The ratio

$$\frac{\text{time for cotton solution}}{\text{time for glycerin}} = \text{specific viscosity}$$

The particular glycerin-water mixture was selected because its time of flow is about the same as that of a cuprammonium solution of cotton that has been damaged to the maximum limit during bleaching.

Another way to express the flow of a liquid is in terms of absolute viscosity. The absolute viscosity of a liquid is expressed in poises, or more frequently in centipoises (0.01 poise). A poise is a value involving force, time and area.

$$\text{poise} = \frac{(1\text{ dyne})(\text{second})}{\text{sq cm}}$$

That is, it is the result of a force of 1 dyne acting for 1 second on 1 sq cm. It can also be evaluated in terms of mass, time, and distance.

$$\text{poise} = \frac{1\text{ gm}}{(\text{second})(\text{cm})}$$

That is, it is a mass of 1 gm acting for 1 second over a distance of 1 cm.

The fluidity of a liquid is the reciprocal of the absolute viscosity, that is, the viscosity when it is expressed in poises. This method has been adopted by British cotton research workers. In a qualitative way, the more viscous a solution is, the less fluid it will be. We know that the cuprammonium viscosity of cellulose decreases as the average chain length is shortened by some modifying treatment, and so such chain shortening should be evidenced by an increase in fluidity.

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[2] *J. Textile Inst.*, **19**, T77 (1928).

The copper number of cellulose is a measure of its reducing power. It is the number of grams of reduced copper obtained from 100 gm cellulose by the action of Fehling's solution (or a modified Fehling's solution). When cellulose is degraded by acid hydrolysis or oxidation, aldehyde groups or potential aldehyde groups are formed. Fehling's solution is essentially an alkaline solution of cupric oxide, CuO, which yields cuprous oxide, Cu_2O, a reddish brown solid, when reduced. The more aldehyde groups there are in a particular sample of cellulose, the more cuprous oxide will be formed, so that a quantitative determination of the Cu_2O formed when the sample is boiled with Fehling's solution is a direct measure of the extent of any aldehyde-forming degradation. If cotton has been overbleached, a light reddish brown stain will be deposited on it when it is boiled with Fehling's solution. The copper number of raw cotton varies with its source, e.g., American cotton, 0.68–1.09, Egyptian cotton, 0.93–1.16; and Indian cotton, 1.54–2.97. However, if raw cotton is very carefully purified, the copper number is 0.05–0.08. This indicates that the impurities in raw cotton have some reducing power. Ordinary commercial cotton has a value of about 0.3. Values for oxidized cotton (where the consumption of oxygen is as high as 0.32%) run from 0.4 to 6.0. Directions for the laboratory determination of the copper number will be found in *Textile Chemistry in the Laboratory.*

The textile chemist is interested in the very first stages of degradation reactions, such as hydrolysis and oxidation. It is obvious that if cellulose chains are broken during such reactions, a loss in strength will occur. Our methods for measuring tensile strength of yarns and fabrics are not very sensitive, and often chemical damage has been done to cloth before its strength is decreased enough to be measured. Determinations of viscosity and copper number are much more sensitive, and they may be used to predict approaching damage before it really occurs.

SOLVENTS FOR CELLULOSE

Cellulose is noted for its great insolubility. It resists the action of all common solvents even at high temperatures for a long time.

You may read that cotton will dissolve in concentrated sulfuric acid, but this is a wrong use of the word dissolve, because cotton is not soluble in H_2SO_4. It disappears, but it is completely destroyed, and cellulose can never be precipitated or recovered from the solution. If we dissolve sugar in water we can always get the sugar back, but if cellulose is "dissolved" in concentrated acid we can never get the cellulose back. Strong solutions of zinc chloride are also said to dissolve cellulose, but actually the effect of zinc chloride is to cause swelling, peptizing, and finally hydrolysis.

However, there are a few solvents which will dissolve cellulose, and the cellulose can be regenerated from these solutions. These solvents are the copper amino hydroxides, the most important of which are ammoniacal cupric hydroxide, copper tetramino hydroxide, cuprammonium hydroxide, and cuprammonium or Schweitzer's reagent. Its formula is $Cu(NH_3)_4(OH)_2$, and it is essentially the result of dissolving cupric hydroxide in ammonium hydroxide and contains the characteristic deep blue copper ammonia ion. A similar compound has been made by the reaction of molecular equivalent amounts of ethylenediamine and copper sulfate. The solution is probably a complex with the formula

$$Cu(H_2N{-}CH_2{-}CH_2{-}NH_2)(CuSO_4)_2$$

Either of these nitrogen compounds will dissolve cellulose, even though it is very highly polymerized, as it is in native cotton.

The word dissolve is still not precisely correct, because the reaction is more a matter of dispersion than solution. We had better say that cellulose is dispersed in cuprammonium hydroxide. However, the two terms are used interchangeably. Ordinary Schweitzer's reagent will dissolve up to 6% cotton in a few hours at 5° C, and it is possible to get as much as 8% dispersed.

The solvent action of Schweitzer's reagent on cellulose is the basis for the manufacture of cuprammonium rayon and therefore is of more than academic interest. We shall discuss some of the factors that govern the reaction and show the probable chemical reactions that occur.

When cotton is immersed in cuprammonium hydroxide, the first thing that is noticed is a definite swelling of the fibers, which causes a radical disintegration of the fiber structure. However, these separated structural fragments are still visible. The next thing that happens is a dispersion of these visible fragments into microscopic, invisible particles. These particles may possibly be the micelles (bundles of cellulose chains). It is possible that the disintegration may go even farther, to the individual chain molecules. Note that what has happened has been disintegration and not degradation.

The amount of cellulose that can be dissolved is related to the concentration of copper in the Schweitzer's reagent, in the sense that the higher the copper concentration, the more cellulose will be dissolved, up to a certain limit. For example, if concentrations of copper as low as 0.25% are used no cellulose will be dissolved (in fact, not even the initial swelling will occur), but as the concentration of copper is increased, the extent of swelling and dispersion of cellulose increases.

The age of the Schweitzer's reagent is an important factor. It tends to decompose into $Cu(OH)_2$ and NH_3, and this will decrease its solvent property, for even though the concentration of copper is still the same, it will have no solvent action unless it is in the copper tetramine ion. Anything that decreases the concentration of copper or converts it into any form other than the tetramine hydroxide will decrease the solvent power of cuprammonium. If this change in copper progresses far enough, cellulose will be coagulated and precipitated from solution.

The condition of the cotton when it is added to cuprammonium should be taken into consideration. Any treatment which will activate the surface of the cotton will cause it to be dispersed more easily and quickly. Any action that will open up the surface, such as mercerization with alkali or vigorous beating with water, will do this. In either of these treatments the cotton should not be allowed to dry before it is immersed in the cuprammonium.

It is reasonable to expect dispersed cellulose to be much more active toward all reagents than a piece of cotton cloth would be. This is because the solid aggregate is broken into micelles or even farther, and the separate chains are much more accessible to the action of various reagents. Cellulose dissolved in cuprammonium is very susceptible to oxidation; even small amounts of air will cause enough degradation in a few minutes to be evidenced by a decrease in viscosity. If the cellulose is to be regenerated as rayon, such oxidation must be prevented or at least held to a minimum, or the rayon will have a low tensile strength. When making viscosity determinations, one must take all precautions to see that air is excluded, because if air gets into the system the dissolved cellulose will be degraded and the viscosity of the solution will be lowered proportionately. One way in which oxidation can be prevented is by the addition of substances which are more easily oxidized than cellulose, such as glucose.

The viscosity of cellulose solutions is also lowered by the action of light, even in an atmosphere of hydrogen. For this reason such solutions and the solvent itself should be protected from light by keeping them in dark brown bottles.

ACID HYDROLYSIS OF CELLULOSE: HYDROCELLULOSE

We have already discussed the hydrolysis of cellulose in a brief way (page 127) and have learned that long chains are broken at the glycosidic linkages. As a result of chain cleavage, reducing groups are formed, and the viscosity of cellulose solutions is decreased. For practical purposes the important thing is that the cellulose suffers a loss of tensile strength, which is of prime interest to the textile technologist. We are now ready to study in more detail the effect of strong (even though dilute) mineral acids on cellulose (acid hydrolysis), together with the physical and chemical properties of the product resulting from such hydrolysis.

When cellulose is allowed to stand with a strong mineral acid such as H_2SO_4 or HCl, a series of reactions takes place. The point of initial attack is certainly on the surface of the solid phase, at which point cleavage of chains occurs, and we may imagine the surface of the solid becoming covered with a layer or film of partially hydrolyzed cellulose. Let us call this first product of hydrolysis a surface hydrolysate. Now assume that the reaction progresses inward from the surface, attacking the next layer of cellulose. This second layer will suffer its initial attack, but at the same time the first layer will be hydrolyzed further, and the proportion of split chains in it will increase. As hydrolysis progresses it is seen that a very complex mixture of products will result, but always that portion of the cellulose which is on the surface will have been hydrolyzed to the greatest extent.

Names have been applied to substances obtained during the hydrolysis of cellulose. The substances are not pure chemical compounds, but they have some average properties by which they can be identified. We have already called the first product a surface hydrolysate. The second product is cellulose dextrin, which still retains some cellulosic nature. The next product is dextrin, and by this time the cellulosic properties have been lost, but the colloidal properties are retained. Dextrin is soluble in water to form somewhat mucilagenous solutions. Further hydrolysis yields a group of polysaccharides which are crystalline and so simple, as compared with cellulose, that they are easily soluble in water. The final product is glucose.

It is to be understood that cellulose is not hydrolyzed in definite complete steps; that is, it is not all converted into cellulose dextrin and then all of it still farther to dextrin. On the contrary, it is possible for some portions of solid cellulose to be hydrolyzed to a water-soluble form, and other portions to be unchanged. Remember that the attack progresses from the surface inward.

We might express the course of hydrolysis by the following equation

$$(C_6H_{10}O_5)_n + HOH = (C_6H_{10}O_5)_r + (C_6H_{10}O_5)_s$$

where r and s are smaller than n.

Then

$$(C_6H_{10}O_5)_r + HOH = (C_6H_{10}O_5)_p + (C_6H_{10}O_5)_q$$

where p and q are smaller than r. As hydrolysis proceeds, shorter chains are formed in which the number of anhydroglucose units gets smaller and smaller. The number of these units, represented by n, r, s, p, q, etc., are unknown until the stage of the simple sugars is reached, after which the subscript letters may be replaced by definite numbers, and finally glucose is formed.

$$(C_6H_{10}O_5)_2 + HOH = \underset{\text{(glucose)}}{2C_6H_{12}O_6}$$

As students of textile chemistry, we are interested only in the first stages of hydrolysis, during which time cotton cloth or yarn is attacked and weakened. When a point is reached beyond which the material loses its fibrous structure, it is no longer a textile problem.

For some time it was thought that the product of the initial attack was a homogeneous substance, and it was called hydrocellulose. Now we know that there is no such homogeneous product, but the name hydrocellulose is still retained. It is the name applied to cellulose that has been only partially hydrolyzed and has not lost its fibrous structure. It is a complex mixture of unchanged cellulose and shortened chain molecules, together with more degraded substances which have no cellulosic properties whatever. Some of these may even be soluble in water, so that the material (cotton cloth) may retain its fibrous form but yet have lost some weight, due to partial solubility.

It would seem that if acid hydrolysis of cellulose causes such disintegration it would be very undesirable and should be avoided as much as possible. And yet sometimes it is very desirable. For example, when wool is "carbonized" to remove small particles of vegetable matter clinging to it, it is heated with sulfuric acid, for the purpose of destroying the vegetable matter, and one method for making wool shoddy from mixed goods destroys cotton fibers by acid hydrolysis.

REACTIONS OF HYDROCELLULOSE

Since hydrocellulose is a mixture the composition of which depends upon the extent of hydrolysis and varies with several factors, its properties should vary considerably. However, the products of hydrolysis have certain properties in common, and a mixture of them will have the same property, but its magnitude will vary.

One thing common to all of the products of hydrolysis is aldehyde groups, the relative number of which depends on the extent of hydrolysis. Therefore, hydrocellulose will reduce Fehling's solution and have a copper number (page 130); it will react with phenylhydrazine, an aldehyde reagent; it will turn yellow when heated with dilute alkali (a property of simple sugars having a potential aldehyde group). The size of the copper number of hydrocellulose is a fairly good measure of the extent of acid degradation.

Using the copper number as such a measure, Birtwell, Clibbens, and Geake[3] arrived at some conclusions about the rate of hydrolysis of cellulose by strong mineral acids. When a certain acid is used at a constant temperature, the extent of hydrolysis (the copper number) is 50% larger when the time is doubled. For example, if a cotton has a copper number of 1.6 after a 1-hour treatment, the value will be 2.4 after a 2-hour treatment. The effect of temperature (with constant time) shows that the copper number becomes 2.3 times as large for each 10° rise in temperature between 20° C and 100° C.

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[3] *J. Textile Inst.*, **17**, T161 (1926).

Another common property of hydrolytic products is that they have shortened chain molecules, and therefore the viscosity of hydrocellulose solutions in cuprammonium hydroxide will be lower than cellulose solutions.

Hydrocellulose is more sensitive to heat than cellulose, and it will start to scorch at about 110° C. A simple test which will show that cotton cloth has been damaged by acids is to iron it with a hot iron. Hydrolyzed areas will scorch sooner than unhydrolyzed areas.

Another important property of hydrocellulose is its partial solubility in hot dilute alkali. As cellulose chains are shortened, a point is reached where the molecule becomes soluble in hot dilute NaOH. Therefore, that portion of hydrocellulose which dissolves in hot alkali has been hydrolyzed beyond this point, and the alkali solubility must be a quite accurate qualitative measure of degradation.

OXIDATION OF CELLULOSE: OXYCELLULOSE

The problems arising from the oxidation of cellulose must be met and understood by the textile chemist whenever it is necessary to bleach cellulosic materials, because bleaching is an oxidation reaction. All reagents that might be used for the bleaching of cotton, linen, wood pulp, paper, etc., are oxidizing agents. It appears that the small amount of coloring matter associated with native cellulose can be converted into colorless substances by oxidation.

One of the major control problems in the cellulose and allied fields comes from the fact that, when bleach liquor is used for whitening cellulose, it is almost impossible to stop the reaction at the point of sufficient bleaching, because cellulose itself is easily oxidized. The structural formula for cellulose on page 125 shows that each anhydroglucose unit of cellulose contains three alcohol groups, one primary and two secondary groups. It is well known that alcohols are oxidizable, the primary alcohols to aldehydes and acids, and the secondary alcohols to ketones. So it is seen that cellulose should react with oxidizing agents, and that the products of such oxidation should function in different ways because of the various functional groups which may result from oxidation. The oxidation of cellulose is not a simple matter, but rather it is very complex, and the product of the oxidation is a heterogeneous, complex mixture. This product has been called *oxycellulose,* but it must be clearly understood that oxycellulose is not a pure chemical compound with a definite structure or molecular weight, nor does it have strictly reproducible properties.

Because of the importance of the oxidation of cellulose, a great amount of research work from the purely scientific standpoint has been done in this field. All types of cellulose have been used, together with all sorts of oxidizing agents under all sorts of conditions, and the products examined in various ways. These experimental oxidations have been carried to different extents, and in many cases have gone far beyond the realm of textiles to a point where the fibrous nature of the material has been entirely lost. At such a point oxycellulose is a nonfibrous, amorphous, powdery, friable white solid. Of course when oxidation goes this far it is no longer a textile problem, and we are really interested only in the earliest stages of oxidation, which would be encountered in the bleaching of cotton.

Most oxidizing agents will oxidize any or all of the alcohol groups of cellulose with which they come into contact. Unruh and Kenyon[4] point out that there are six points of oxidative attack:

1. Attack at carbons 2 or 3, or both, oxidizing these secondary alcohol groups to ketones, without breaking the ring.
2. Oxidation at both carbons 2 and 3 to form aldehydes, with a simultaneous rupture of the ring.
3. Oxidation of the primary alcohol group at carbon 6 to an aldehyde.

Any of these three oxidations will yield an oxycellulose, known as the reducing type, with almost no carboxyl groups in it. It will be characterized by a high copper number.

4. Further oxidation of aldehyde groups at carbons 2 and 3 to carboxyl groups.
5. Oxidation of the carbon 6 alcohol group to a carboxyl group.

These two oxidations will yield a carboxyl type of oxycellulose with very few, if any, reducing groups in it. It will have a high COOH content, as measured by methylene blue absorption.

6. The oxidation may result in oxidation of alcohol groups at

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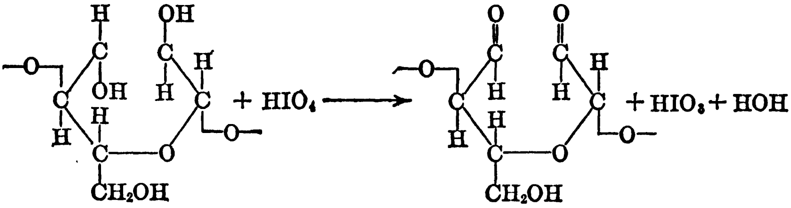
[4] *Textile Research J.*, **16**, 1–12 (1946).

#2 and 3 to aldehyde groups, followed by further oxidation of one of them to COOH, leaving the other one as CHO. Such an oxycellulose will have a high COOH content and also a high reducing property.

A nonspecific oxidizing agent might act in any of the preceding ways so that we may expect oxycellulose to show the properties of a carbonyl compound (especially aldehydic), a carboxylic compound, and very probably a compound with a lower degree of polymerization due to chain rupture; hence oxycellulose will have lower cuprammonium viscosity than unmodified cellulose.

There are two oxidizing agents that seem to be specific in their action. These are periodic acid and nitrogen dioxide. Since Jackson and Hudson[5] discovered that the oxidative attack on polysaccharides by periodic acid is specifically confined to α-β glycol arrangements, a large amount of research has been done in the field of periodic acid oxidation. Some of the more important contributions have been made in England by Davidson,[6] and in the United States by Michell and Purves,[7] Rutherford, Miner, Martin, and Harris,[8] and in unpublished work from the laboratory of Michigan State College. When cotton cellulose is treated with dilute solutions of periodic acid, the 2 and 3 secondary alcohol groups are oxidized to two aldehydes (together with an opening of the ring), but the 6 primary alcohol is not affected. The amount of glycosidic cleavage during periodic acid oxidation is small, but note that the ring structure is ruined and the tensile strength of cellulose fibers is reduced by a fraction equivalent to the proportion of such strength contributed by the ring structure.



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[5] *J. Am. Chem. Soc.*, **59**, 2049 (1937), and **60**, 989 (1938).

[6] *J. Textile Inst.*, **29**, T195 (1938); **31**, T81 (1940); **32**, T25 and T109 (1941).

[7] *J. Am. Chem. Soc.*, **64**, 589 (1942).

[8] *J. Research Natl. Bur. Standards*, **29**, 131 (1942).

The oxidation of cotton cellulose by nitrogen dioxide gas is being studied in the Eastman Kodak laboratories by Kenyon and associates. They have found that this oxidizing agent specifically attacks the 6 primary alcohol groups of cellulose, converting them into carboxyl groups. The product appears to be a new type of oxycellulose, the chief difference being that the cotton retains its soft fibrous character and does not become friable, even after extensive oxidation. These facts indicate that there is very little cleavage of glycosidic linkages and very little rupture of the cross-links between chains.

It is logical to assume that the mechanism of the oxidation of cellulose consists of an attack on the surface, followed by an inward progressing attack on succeeding layers. If the oxidation is accompanied by chain splitting, the outer layers will have shorter chains than the inner layers. The outer layers will also have more aldehyde and carboxyl groups than the inner layers. This mechanism is analogous to the acid hydrolysis of cellulose (page 133), and we must then conclude that oxycellulose is a heterogeneous, complex mixture of extensively oxidized cellulose, slightly oxidized cellulose, and unoxidized cellulose, the highest oxidation products being on the surface.

REACTIONS OF OXYCELLULOSE

On the basis of the structure of cellulose, oxycellulose should contain the carbonyl groups of aldehydes and ketones, carboxyl groups, and shorter chains. The aldehyde portion should make it a reducing agent; both aldehyde and ketone groups should give to oxycellulose the usual carbonyl reactions; the carboxyl groups should make it behave like an acid; and the presence of shorter chains should result in cuprammonium solutions with lower viscosities.

There are four reactions of oxycellulose which show the presence of aldehyde group. First and most important is the reaction with Fehling's solution, in which oxycellulose reduces Fehling's solution and precipitates cuprous oxide (page 38). The determination of copper numbers is based on this reaction. One might think that the size of the copper number would be a measure of the amount of oxygen consumed during oxidation, but this is not always true. Some oxycelluloses give copper numbers that are much lower than would be expected. This will be discussed later (page 143). Some ketone sugars in which the ketone group is adjacent to a secondary alcohol group will reduce Fehling's solution, and so part of the reducing property of oxycellulose may be due to the oxidation of either 2 or 3 secondary alcohol groups in the anhydroglucose ring. We may use the Fehling's solution reaction for detecting the presence of overbleached areas on cotton goods.

The reaction of oxycellulose with alkali is a complex one, and there has been some confusion regarding the alkali stability of oxidized cellulose. Unruh and Kenyon[9] divide oxycelluloses into three types:

1. Those that have the same glucosidic structure as the original cellulose and yet are soluble in NaOH, owing to their short chain length. These are the alkali-susceptible type.
2. The alkali-soluble type, in which the degree of polymerization is comparable with the original cellulose but the COOH content is high.
3. Those that dissolve in NaOH by fragmentation caused by alkaline decomposition of glucose units and the changed structure (during oxidation). These are the alkali-sensitive type.

When oxycellulose is boiled for a short time with dilute (3%) NaOH, it is colored a golden yellow. This reaction is characteristic of the simple reducing sugars and therefore is evidence of the existence of aldehyde groups in oxycellulose. On longer boiling with NaOH, part of the oxycellulose dissolves, and the solution has reducing properties. This seems to mean that the alkali solubility of slightly oxidized cellulose may be due to aldehyde groups. This has been proved true at least in periodic acid oxycellulose, by Davidson,[10] Rutherford, Miner, Martin and Harris,[11] and Goldfinger, Mark, and Siggia.[12] In the early stages of periodic acid oxidation, it appears that all of the alkali sensitivity can be attributed to the dialdehyde, and, in fact, when these aldehyde groups are converted into carboxyl groups, the alkali sensitivity disappears. This periodic acid oxycellulose has been stabilized by Reeves[13] by treating the material with sodium chlorite at a *p*H of 4. On the other hand, the alkali solubility of nitrogen dioxide oxycellulose seems to be a function of the number of carboxyl groups. However, note that these oxycelluloses are oxidized far beyond the early stages.

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[9] *Textile Research J.*, **16**, 1–12 (1946).

[10] *J. Textile Inst.*, **29**, T195 (1938), and **32**, T25 (1941).

[11] *J. Research Natl. Bur. Standards*, **29**, 131 (1942).

[12] *Ind. Eng. Chem.*, **35**, 1083 (1943).

[13] *Ind. Eng. Chem., Ind. Ed.*, **35**, 1281 (1943).

When cotton is oxidized with hypochlorites, the alkali solubility runs parallel to the oxygen consumption expressed in grams oxygen used per gram of cotton.[14]

The presence of aldehyde groups in oxycellulose can be demonstrated by means of Schiff's reagent if the oxidation is sufficient. This is not a very sensitive test, but if cotton is badly overbleached it will form a pink color with Schiff's reagent.

If oxycellulose contains carboxyl groups it should behave like a weak organic acid. This has been demonstrated in various ways, most of which can be used for determining the number or percentage of COOH groups in oxycellulose. These methods can be divided into four groups: direct titration, indirect titration, decarboxylation, and basic dye absorption.

The carboxyl groups in oxycellulose can be determined by titrating an aqueous suspension of the solid with 0.01 *N* NaOH, using phenolphthalein as an indicator. As hydrocellulose has a reducing property just like oxycellulose, one cannot distinguish between these two kinds of modified cellulose by means of a value such as the copper number. However, direct titration seems to offer such a possibility. The percentage of COOH groups in hydrocellulose has been found to be much smaller (about the same as unmodified cellulose) than in oxycellulose.

A modification of direct titration can be used with oxycelluloses having a high COOH content, such as some of the nitrogen dioxide oxycelluloses. Since they are completely soluble in NaOH, they may be dissolved in a measured excess of standard NaOH, and the excess alkali titrated with standard acid.

These high COOH oxycelluloses may also be dissolved in pyridine and the solution titrated directly with standard NaOH.

Neale and Stringfellow,[15] from theoretical considerations, claim that direct titration in the presence of a large excess of NaCl gives more exact results.

An indirect titration method has been suggested by Ludtke in which oxycellulose is treated with an excess of calcium acetate. The presence of a large concentration of acetate ions forces the liberation of acetic acid in an amount equivalent to the amount of carboxyl in the oxycellulose, according to the following equation:

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[14] Hartsuch and Alvord, unpublished.

[15] *Trans. Faraday Soc.*, **33**, 881 (1937).

$$2RCOOH + Ca(OAc)_2 \longrightarrow (RCOO)_2Ca + 2HOAc$$

The acetic acid can then be titrated with standard NaOH. This method has been modified and improved by Yackel and Kenyon.[16]

Oxycellulose can be decarboxylated by boiling with a 12% solution of HCl, liberating CO_2 in an amount equivalent to the carboxyl content. Simultaneously with the liberation of CO_2 a certain amount of furfural is obtained, but it is not formed in stoichiometric amounts and cannot be used for determining the carboxyl content of oxycellulose. However, the yield of CO_2 is quantitative and is a direct measure of COOH groups. Because of this we have another method for distinguishing between hydrocellulose and oxycellulose. Heuser and Stockigt[17] found that cotton and hydrocellulose contain from 0.03 to 0.04% COOH groups, whereas various oxycelluloses which they investigated ran from 0.6 to 1.3% COOH groups. More extensive oxidation would of course give larger yields of CO_2.

When oxycellulose is treated with dilute solutions of basic dyes, it absorbs them and holds them during washing. The basic dyes are in solution as salts of very weak acids and hence will react with carboxyl groups in oxycellulose, so that an amount of dye equivalent to the carboxyl content is absorbed. The dyestuff most used for this purpose is methylene blue, and the methylene blue number of oxidized cellulose is important for evaluating the extent of oxidation to the carboxyl stage. Hydrocellulose will not absorb as much methylene blue as oxycellulose.

Shorter average chain length in oxycellulose can be shown by the lower viscosities of cuprammonium solutions, and by the complete solubility of highly oxidized cellulose in alkali. There is no straight-line relation between viscosity and alkali solubility, but in general those oxycelluloses with low viscosities have high (or complete) alkali solubilities.

Another property of oxycellulose that is of practical use is its behavior when heated. Like hydrocellulose, it scorches more easily than unmodified cotton. Hydrocellulose shows scorch at about 110° C, oxycellulose at about 140° C, and cotton at 170° C.

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[16] *J. Am. Chem. Soc.*, **64**, 121 (1942).

[17] *Cellulosechemie*, **3**, 62 (1922).

TYPES OF OXYCELLULOSE

The work of Birtwell, Clibbens, Geake, Ridge, and others[18] working in the laboratories of the British Cotton Industry Research Association established the fact that there are two definite types of oxycellulose, the characteristics of which depend upon the *p*H of the oxidizing solution. In their extensive investigation they worked under controlled conditions of concentration, *p*H, time, and temperature. They studied various oxidizing agents, e.g., chlorine water, potassium permanganate, and alkaline hypobromite, using five different concentrations but the same amount of total available oxygen for each oxidizing agent. The weight of cotton used and the volume and concentrations of solutions were adjusted so that, when the entire oxidizing power of each reagent was used up, it would correspond to an oxygen consumption of 0.032, 0.064, 0.096, 0.16, and 0.32 per cent, based on the weight of dry cotton. This would result in considerably overbleached cotton, as the usual consumption of oxygen in commercial bleaching is about 0.02%. After the oxidations were completed, the properties of the oxycelluloses were studied, the ones in which we are interested being copper number, methylene blue number, and alkali solubility.

It was found in general that the chlorine water oxycelluloses had high copper numbers and high alkali solubility with a large amount of yellow color, but the methylene blue absorption was relatively low. On the other hand, the oxycelluloses prepared by oxidation with alkaline hypobromite had high methylene blue numbers but low copper numbers, low alkali solubility, and only a small amount of yellow color. The properties of the permanganate oxycelluloses were intermediate. Some actual results obtained after an oxygen consumption of 0.32% are given herewith.

	Copper Number	Methylene Blue Number
Chlorine water oxycellulose	6.0	0.6
Permanganate oxycellulose	1.8	1.3
Alkaline hypobromite oxycellulose	0.4	2.7

It was found that the loss in weight when the oxycelluloses are boiled with alkali is determined by the copper number. Thus, those with high copper numbers lose much more weight than those with high methylene blue numbers. It is interesting to note the effect of alkali boiling on the copper numbers and methylene blue numbers of the oxycelluloses produced in alkaline medium (those with high methylene blue numbers and low copper numbers). A particular one which had a copper number of 0.5 and a methylene blue number of 2.95 was refluxed for eight hours with 2% NaOH solution, after which the copper number was 0.05 and the methylene blue number was 2.67. This shows that the methylene blue number is affected very little by alkali boiling, but the copper number is very greatly diminished, so much so that one could not distinguish the residue from alkali boiling from the original unoxidized cellulose.

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[18] *J. Textile Inst.*, **15**, T27 (1924); **16**, T13 (1925); **17**, T145 (1926); **18**, T135, T277 (1927).

TABLE 20

OXYCELLULOSES MADE AT DIFFERENT *p*H*

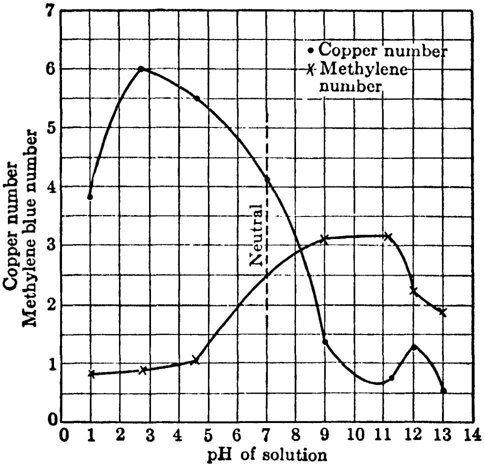
(Total oxygen consumed = 0.32% at 25° C)

*p*H	Copper Number	Methylene Blue Number
1	3.79	0.81
2.7	6.00	0.90
4.6	5.50	1.04
7	3.64	2.23
9	1.37	3.20
11.2	0.65	3.26
12	1.31	2.28
13	0.54	1.91

* Birtwell, Clibbens, and Ridge, *J. Textile Inst.*, **16**, T30 (1925).

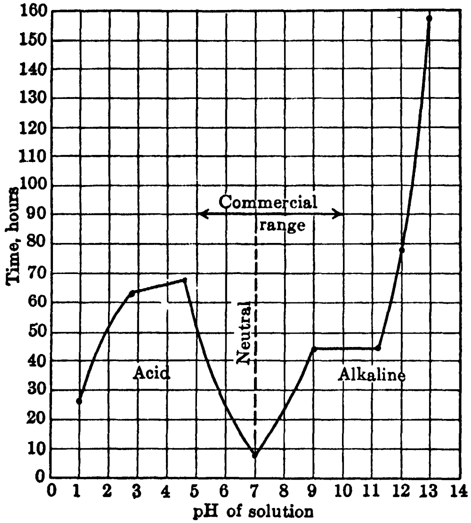
In the study of the effect of hydrogen ion concentration on the properties of oxycellulose, Birtwell *et al.* used a solution of sodium hypochlorite of such strength that its complete reduction was equivalent to 0.32% oxygen consumption based on the dry weight of cotton used in the experiment. The solutions of sodium hypochlorite were suitably buffered so that a wide range of *p*H was obtained, running from 1.0 to 13. The proper amount of cotton and oxidizing solution was put into jars and kept at 25° C until the entire amount of oxygen (0.32%) had been consumed. The time required varied from 2 to 14 days. The copper number and methylene blue number of the oxycelluloses prepared in this way are given in Table 20.

In the graph below the two numbers are plotted against the *p*H, and the shape of the two curves shows the oppositeness of the two types of oxycellulose. Note that the maximum of one is on the acid side and the maximum of the other is on the alkaline side. For example, the maximum in the copper number curve is at *p*H 2–4, whereas the maximum on the methylene blue number curve is at *p*H 9–11. On the copper curve, the value at *p*H of 12 is decidedly out of line. Aside from this one discrepancy, each curve has a maximum on each side of which the values decrease.



Note that in both types of oxycellulose the greatest change in the two numbers, that is, the change from maximum to minimum, occurs in the narrow range of *p*H between 5 and 9. Note also that the two curves cross at approximately the neutral point (*p*H 7). Suppose cotton has consumed more than 0.32% oxygen. Both numbers would then be larger, and if the oxidation were carried out at a *p*H of about 7, either number would indicate the extent of oxidation. But if the *p*H of the oxidizing solution were off the neutral point only a small amount, the determination of one number would not be sufficient to indicate the extent of oxidation, and both values would have to be determined. When the analyst is required to investigate cloth damage that may have been due to oxidation, he should always determine both copper number and methylene blue number.

In their investigation of the rate of hypochlorite oxidation of cotton, Clibbens and Ridge[19] made valuable contributions to the chemistry of bleaching. They treated cotton with solutions of sodium hypochlorite suitably buffered so as to have a range of *p*H values from 1 to 13. They determined the time required for the consumption of one-half of the available chlorine and took that as a measure of the rate of oxidation. The results are shown in Table 21 and the accompanying diagram.



Let us see what this diagram tells us. We see that hypochlorite oxidation in a very strongly alkaline solution (*p*H 13) is very slow, but there is a rapid increase in the rate as the alkalinity is decreased from *p*H 13 to *p*H 11. Then the rate remains about the same until a *p*H of 9 is reached, after which the rate increases until it reaches its maximum at the neutral point (*p*H 7). If we start with the strongly acid hypochlorite (*p*H 2), the same type of change is seen to occur. The slowest rate is at a *p*H of 4, and then, as the acidity decreases, the rate increases until it again reaches a maximum at the neutral point. The range of *p*H in technical liquors used for bleaching cotton is from 5 to 9.5. Table 21 and the diagrammatic curve tell us that in this range one encounters the fastest rates of reaction, and thus the possibility of damage by overbleaching is great. Any proper control of hypochlorite bleaching should rigidly avoid allowing the bath to become neutral. That is, commercial bleachers must keep away from the neutral point, and the control of the *p*H of bleach liquors is becoming more and more recognized as very important.

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[19] *J. Textile Inst.*, **18**, T135 (1927).

Let us summarize the foregoing discussion on types of oxycellulose. There are two types: (*a*) the reducing type, which is formed by oxidation in acid medium and is characterized by high copper numbers, great alkali solubility, large amount of yellow color, and low methylene blue absorptions; and (*b*) the nonreducing or carboxyl type, which is formed by hypochlorite oxidation in alkaline medium and is characterized by high methylene blue absorption, low copper numbers, and low alkali solubility with small amounts of yellow color formation. Further conclusions are that, for the same oxygen consumption, different oxidizing agents yield oxycelluloses with different properties, and that the rate of oxidation is a function of the *p*H of the oxidizing liquor.

TABLE 21

RATE OF HYPOCHLORITE OXIDATION*

(Time of one-half oxygen consumption)

*p*H of Bath	Hours
1	27
2.7	63
4.6	67
7	9
9	44.5
11.2	44
12	77.5
13	158

* Clibbens and Ridge, *J. Textile Inst.*, **18**, T135 (1927).

ESTERS OF CELLULOSE

We shall discuss the nitrates (formerly important in rayon manufacture and still important in the field of explosives), the acetates (important in the manufacture of acetate rayon, such as Celanese), and the xanthates (used for making viscose rayon, which is produced in far greater amount than any of the other rayons).

Esters may be considered as derivatives of acids, either mineral or organic, in which the acid hydrogen has been replaced by some organic radical. In the preparation of an ester of a mineral acid, an alcohol can react with the mineral acid itself,

$$\mathrm{ROH} + \mathrm{HONO_2} \longrightarrow \mathrm{RONO_2} + \mathrm{HOH}$$

However, in the preparation of an ester of an organic acid we may react an alcohol with the organic acid itself, with its acid chloride, or its acid anhydride.

$$\mathrm{R'COOH} + \mathrm{ROH} \longrightarrow \mathrm{R'COOR} + \mathrm{HOH}$$

$$\mathrm{R'COCl} + \mathrm{ROH} \longrightarrow \mathrm{R'COOR} + \mathrm{HCl}$$

$$\mathrm{(R'CO)_2O} + 2\mathrm{ROH} \longrightarrow 2\mathrm{R'COOR} + \mathrm{H_2O}$$

In our study of the hydrolysis and oxidation of cellulose, we emphasized the topochemical nature of the reaction. The same thing is true of the esterification of cellulose with acids or acid anhydrides. In order for esterification to take place, it is necessary for the reagent to come into contact with alcohol groups. This is complicated in the esterification of cellulose because of its micellular, chain-bundle structure. Alcohol groups on the surface of micelles or in the outer layer of cotton fibers may be reacted easily because they are exposed, but it is conceivable that further esterification may be slowed up or even prevented because of the inability of the reagent to reach interior alcohol groups. If an extensive reaction is desired, something must be done to open up the interior and make the interior alcohol groups more accessible. This can be accomplished by the use of swelling agents, such as strong sulfuric acid or salts like zinc chloride. If the cellulosic material is swollen enough, the esterification may take place almost simultaneously at all points. All efficient methods for the preparation of cellulose esters make use of so-called starters or activators, which are usually good swelling agents.

THE NITRATES OF CELLULOSE

At the top of this page is shown the esterification of nitric acid with a simple monohydric alcohol, but if the alcohol were to have three OH groups, a similar reaction would take place, the only difference being that three molecules of $\mathrm{HNO_3}$ would take part in the reaction. This can be shown in the reaction between nitric acid and glycerol:

$$\mathrm{C_3H_5(OH)_3} + 3\mathrm{HONO_2} \rightleftarrows \mathrm{C_3H_5(ONO_2)_3} + 3\mathrm{HOH}$$

Note two things about this reaction: (1) it is reversible, so that the formation of ester will cease when sufficient water has been formed, and (2) one molecule of water is formed for each OH group reacting. In the actual preparation of esters of nitric acid, some dehydrating agent is always used to remove the water formed during the reaction.

As cellulose contains three OH groups per glucose unit, we can react it with HNO_3 as we do glycerol. If we write the anhydroglucose unit $C_6H_{10}O_5$, so as to show the three OH groups, it will be $C_6H_7O_2(OH)_3$, and the equation will be

$$C_6H_7O_2(OH)_3 + 3HONO_2 \rightleftarrows C_6H_7O_2(ONO_2)_3 + 3HOH$$

Correctly speaking, the product should be called cellulose trinitrate, and the reaction, esterification. However, the common name for the product is nitrocellulose, and the reaction is called nitration. This is not correct because nitration is a reaction by which nitro groups, NO_2, are introduced. The group introduced into the cellulose molecule is the nitrate group (ONO_2), and the product should be thought of as a nitrate of cellulose or cellulose trinitrate. However, the incorrect names are so widely used that they will appear frequently in this book.

Let us look at the situation that exists in a reaction mixture in which cellulose is being nitrated with concentrated nitric acid, with concentrated sulfuric acid as a dehydrating agent. In the first place, the reaction is a slow one, and it is inconceivable that all three of the cellulose OH groups would be nitrated at the same time. So we must consider that the first product is a mononitrate in which only one OH group has been acted upon. As the reaction progresses a dinitrate will be formed, and finally a trinitrate. These reactions are shown below.

$$C_6H_7O_2(OH)_3 + HONO_2 \rightleftarrows \underset{\text{(the mononitrate)}}{C_6H_7O_2(OH)_2(ONO_2)} + HOH$$

$$C_6H_7O_2(OH)_2(ONO_2) + HONO_2 \rightleftarrows \underset{\text{(the dinitrate)}}{C_6H_7O_2(OH)(ONO_2)_2} + HOH$$

$$C_6H_7O_2(OH)(ONO_2)_2 + HONO_2 \rightleftarrows \underset{\text{(the trinitrate)}}{C_6H_7O_2(ONO_2)_3} + HOH$$

The reaction is carried out in the presence of a large excess of acids that may hydrolyze the esters, thus converting trinitrates into dinitrates, etc. This would occur if the reaction mixture were too hot or if it were allowed to stand for too long a time. There is also a chance that oxidation might take place, because nitric acid is an oxidizing agent. It is seen that the product of the nitration of cellulose will be a complex mixture.

The extent of nitration of cellulose is expressed in terms of the percentage of nitrogen in the product. For example, the trinitrate is $C_6H_7O_2(ONO_2)_3$, with a molecular weight of 297, of which 42 grams is nitrogen (3 × 14). Then 42 ÷ 297 is 14.1%. The three nitrates are mono- = 6.8% N, di- = 11.1% N, and trinitrate = 14.1% N. These are the nitrogen contents of the pure nitrates, but it should be clear that no cellulose nitrate is a pure compound. They are all mixtures of mono-, di-, and trinitrates, but they all have certain percentages of nitrogen. The different cellulose nitrates are used for various purposes, and manufacturers of these commercial products have found that a specific, fairly narrow range of nitrogen content is necessary for each particular product. Therefore, controls are imposed on the manufacturing operations so that the product is reproducible; that is, it will always have about the same nitrogen content. For example, nitrocellulose (guncotton), used in explosives, contains 12.5 to 13.7% N; that used for making lacquers, 11.5 to 12.2% N; and that used in various plastics, from 10.5 to 11.5% N.

CELLULOSE ACETATE

Cellulose acetate was first prepared by Shutzenberger in 1865, but was put to no commercial use until 1903, when the Miles patents were granted (page 154). After that time it began to take a small place in the industrial field, but very little development was made until World War I, when it was found that "dopes" of cellulose acetate applied to the wings of airplanes left a very good protective coating. Large acetylating plants were built to produce this material. At the close of the war it was necessary to find new uses and new markets for cellulose acetate. So successful were these efforts that today we find this cellulose derivative being manufactured in huge amounts for use in various fields such as rayon, plastics, films, adhesives, lacquers, shatterproof glass, etc. Of these fields, rayon is by far the most important, and about 75% of the supply of cellulose acetate is used in the manufacture of rayon.

Cellulose acetate is an ester of cellulose and acetic acid in which the three OH groups of cellulose have been replaced by acetate radicals (the three alcohol hydrogens of cellulose have been substituted by acetyl groups). The esters of cellulose and organic acids are prepared by a general reaction known as acylation, and the reagent used is called an acylating agent. When we go from the general to the particular, to make acetyl cellulose (cellulose acetate), the reaction is called acetylation and the reagent an acetylating agent. Acetic anhydride is the only acetylating agent to be used in the manufacture of cellulose acetate. The reaction is shown below:

$$C_6H_7O_2(OH)_3 + 3(CH_3CO)_2O = C_6H_7O_2(OCOCH_3)_3 + 3CH_3COOH$$

We immediately see a difference between this reaction and the one by which cellulose nitrate is formed. In the present reaction, water is not a product, so that the reaction does not reverse. Furthermore, there is no strong acid present which will hydrolyze either cellulose acetate or cellulose. For these reasons the system is not sensitive to small differences in the concentration of reactants, and the reaction should go straight through to the formation of the triacetate, with very little of the mono- or diacetate in the product. It is claimed that it is impossible to obtain a uniform acetate of low acetyl content which is either the mono- or diacetate.

The acetylation of cotton with acetic anhydride is even more of a topochemical reaction than nitration. The attack starts with the exposed OH groups on the surface of the cotton fiber, and must then progress inward. However, this progress is very slow unless the cotton has been pretreated with some swelling agent to open it up and make it more pervious, and permit the acylating agent to make contact with interior OH groups. Sometimes such an agent is incorporated in the acylating bath, but cellulose acetate can be made in a shorter time and more uniformly if the cotton is swollen before being acetylated.

The convention for expressing the extent of acetylation, or the analysis of a commercial acetate, is in terms of the percentage of acetic acid, or the percentage of acetyl. For example, the triacetate is $C_6H_7O_2(OCOCH_3)_3$, with a molecular weight of 288, and even though there is no acetic acid in it, we know that the hydrolysis of it will yield three moles of acetic acid (wt $3 \times 60 = 180$). One hundred eighty is 62.5% of 288, and so we say that the triacetate contains 62.5% CH_3COOH. In a similar way we can calculate the acetic acid content of the diacetate to be 48%, and of the monoacetate 29%. Let us write the formula for the triacetate $C_6H_7O_5(COCH_3)_3$ to show three acetyl groups with a total weight of 129, which is 44.8% of 288. Thus the acetyl content of completely acetylated cellulose is 44.8%, of the diacetate 35%, and of the monoacetate 21.1%.

There are two general methods for determining the acetic acid content of cellulose acetate, each of which has its modifications for special purposes. The distillation method of Ost and Katayama,[20] modified by Hess,[21] consists of adding an excess of H_2SO_4 to the acetate, allowing it to stand, and then distilling off the acetic acid which is liberated. The distillate is titrated with standard alkali to determine the amount of acetic acid. The saponification or alkaline method hydrolyzes the acetate with a measured amount of alkali, and, after the saponification is complete, the unused alkali is titrated. The alkali disappearing in the saponification is equivalent to the acetic acid in the acetate. The more recent modifications of this method are due to Genung and Mallatt[22] and to Howlett and Martin.[23]

Three materials are necessary for the preparation of cellulose acetate: an acetylating agent (always acetic anhydride), a starter (catalyst), and a diluent (a liquid reaction medium). The purpose of the acetylating agent is obvious; the starter must be a swelling and peptizing agent that will activate the cellulose; the diluent may be a liquid which will dissolve cellulose acetate, or it may be a liquid in which the acetate is insoluble. As we have a choice, we can prepare two types of cellulose acetate. If cotton is acetylated in a diluent such as benzene, the cellulose acetate will be insoluble. The product will retain the same fibrous form as the original cotton, and we shall have a fibrous acetate. On the other hand, if glacial acetic acid is the diluent it will dissolve the cellulose acetate as fast as it is formed. If this solution is diluted with water, the solvent property of acetic acid will be destroyed, and the acetate will precipitate in an amorphous flake form. The fibrous acetate may be used in the academic study of cellulose acetate, but the amorphous acetate is the only one that is manufactured industrially.

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[20] *Z. angew. Chem.*, **29**, 1467 (1912).

[21] *Ann.*, **435**, 65 (1923).

[22] *Ind. Eng. Chem., Anal. Ed.*, **13**, 369 (1941).

[23] *J. Textile Inst.*, **35**, T1 (1944).

When cotton is acetylated under any conditions it is more or less degraded. This can be shown by the decrease in the viscosity of cuprammonium solutions of cellulose acetate. Most of the starters and the preliminary treatments given cotton before acetylation cause degradation and produce shorter chains. When sulfuric acid is used as a catalyst, the degree of polymerization of the acetate is only about 15–20% of the original cotton.

A few statements should be made about the rate of acylation of cotton with acetic anhydride, and the factors that govern it. One of these is the moisture content of the cotton to be acetylated. Experiments carried out by Elöd and Schmidt-Beilenberg[24] with dry cotton, air-dry cotton, and moist cotton in the presence of benzene showed that the time required to form the triacetate from the moist cotton was much shorter than the other periods. After about twelve hours, cellulose acetates with the following acetic acid contents were obtained from cotton with the designated moisture contents:

62.5% acetic acid from cotton with 24.4% H_2O
22% acetic acid from cotton with 6.7% H_2O
10% acetic acid from cotton with 0.1% H_2O

It is thought that water in excess of the normal moisture content of cotton opens up the micellar structure of the cotton and permits the acylating liquid to penetrate more easily and thus react more rapidly. On this assumption, any swelling agent should bring about the same increase in rate of reaction. Acetic acid is a fairly good preswelling agent; it will increase the rate of acetylation about tenfold. Other agents are sulfuric acid and zinc chloride.

Commercial cellulose triacetate is known as primary acetate. It is an amorphous white solid insoluble in water, in dilute acetic acid, in acetone, and in most of the common organic solvents. It will dissolve in chloroform, glacial acetic acid, tetrachloroethane, nitrobenzene, aniline, and pyridine. Chloroform solutions of the primary acetate can be extruded to form filaments, but they are weak and brittle and unsuitable for technical purposes. However, the primary acetate can be converted into a form that is entirely suitable for a great many uses. The process for such conversion was discovered and patented by Miles[25] in 1903–1904. Miles prepared the triacetate in the usual way in glacial acetic acid, but after acetylation was complete, instead of precipitating the acetate from the glacial acetic acid solution, he added a 50% solution of acetic acid containing some sulfuric acid (this is not dilute enough to precipitate the acetate) and allowed it to stand at 50° C for 12 to 14 hours, after which cellulose acetate was precipitated by diluting the solution with water. Miles called this product a secondary acetate. Secondary cellulose acetate has different properties from the primary acetate, most important of which is the fact that it will dissolve in acetone. Miles' secondary acetate has a great advantage over the primary acetate. In the first place, it is soluble in a cheap solvent, and second, when the acetate is regenerated from the acetone solution in filament form, it is soft, flexible, and strong enough to be used as a textile fiber. It was the first really synthetic fiber to be used in textiles.

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[24] *Z. physik. Chem.*, **B25**, 31 (1934).

Cellulose acetates suitable for different purposes contain different amounts of acetyl groups. As a group, the acetone-soluble acetates contain 35.8 to 41.5% acetyl. Those used for making films contain 39.4% to 41.6% acetyl, those for rayon contain 38 to 39.4% acetyl, and those used for plastics 36.5 to 38% acetyl.

When these acetates for special purposes are manufactured, no effort is made to acetylate cellulose to any special extent. For example, if acetate is being made for rayon manufacture, the process is not controlled to put just 38.5% acetyl into the product. All efforts to do this have proved unsuccessful. Instead, cellulose is acetylated completely and then deacetylated to the desired acetyl content. It is this deacetylation that is brought about by the Miles reaction. Formerly it was thought that the acetone solubility of the secondary acetate was due to a disaggregation, a simplification of the molecule, or perhaps a process of chain shortening, but these ideas have been discarded. The question has never been definitely settled, but it is probable that the new solubility properties of the secondary acetate are due to deacetylation, with the accompanying liberation of primary alcohol groups in the carbon 6 position.[26] They demonstrated that deacetylation processes remove acetyl groups from the 6 and the 2 and 3 positions in about equal amounts, and concluded that the acetone solubility depends upon the average numerical amount of acetyl groups per glucose unit and their distribution. It is probable that direct acetylation to 38% acetyl group blocks too many primary alcohol groups, so that the product, even though it has the proper percentage of acetyl groups, does not have enough unacetylated primary alcohol groups. The necessity for free primary alcohol groups in acetone-soluble secondary acetates seems to be confirmed by the fact that this solubility is very much decreased by heating the secondary acetate with glacial acetic acid. The supposition is that primary alcohol groups are re-esterified by this treatment.

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[25] U.S. Patent 838,350.

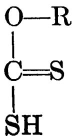
[26] Cramer and Purves, *J. Am. Chem. Soc.,* **61**, 3458 (1939).

CELLULOSE XANTHATE: VISCOSE

The xanthate of cellulose is fully as important, if not more so, as the two cellulose esters just discussed. This is especially true from the textile chemist's point of view, because about 65% of the world's supply of rayon is made by the regeneration of cellulose from cellulose xanthate (see page 221). It is used to a much smaller extent for other purposes, such as films, artificial sponges, bottle caps, and casings for packing ground meat, but by far the most important use is in the field of rayon manufacture.

Cellulose xanthate was discovered by Cross and Bevan in 1892. They found that it could be dissolved in dilute NaOH to form a thick viscous solution to which they gave the name *viscose*. Later it was found that filaments of regenerated cellulose could be made by passing streams of viscose into acid coagulating baths. Eventually such filaments were put on the market as artificial silk under the name viscose silk. Today we know that the production of viscose rayon exceeds the combined production of all other rayons.

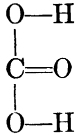
Before starting the study of viscose, we must clarify certain points in the nomenclature of the subject. In the first place, we are considering it as an ester of cellulose. In textile chemistry literature, it is often designated as the cellulose ester of xanthogenic acid (or xanthic acid), but if we look at the structure of xanthogenic acid we shall find that such a designation is incorrect.



$$\begin{array}{l} \mathrm{O{-}R} \\ \mid \\ \mathrm{C{=}S} \\ \mid \\ \mathrm{SH} \end{array}$$

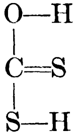
The accompanying formula is the general one for xanthogenic acid, in which R may be any simple alkyl group, such as C_2H_5. Thus the name xanthogenic acid is applied to any acid having this general formula. Note that the acid hydrogen of xanthogenic acid is attached to sulfur. Therefore, an ester of xanthogenic acid would be a compound in which this hydrogen has been replaced by an alcohol radical, such as ethyl, C_2H_5; butyl, C_4H_9; or cellulose, $C_6H_9O_4$. But in viscose we find the $C_6H_9O_4$ group attached to oxygen instead of sulfur, and we note that it exists as a sodium salt in which a sodium atom is attached to sulfur.

It is more logical to consider viscose as a derivative of dithiocarbonic acid instead of xanthogenic acid. Let us look at the relations among carbonic acid, dithiocarbonic acid, and viscose. The syllable thio means sulfur in place of oxygen, and the first two of the following formulas show the two acids:



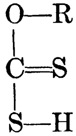
$$\begin{array}{l} \mathrm{O{-}H} \\ | \\ \mathrm{C{=}O} \\ | \\ \mathrm{O{-}H} \end{array}$$

(carbonic acid)



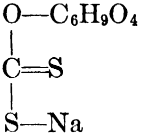
$$\begin{array}{l} \mathrm{O{-}H} \\ | \\ \mathrm{C{=}S} \\ | \\ \mathrm{S{-}H} \end{array}$$

(dithiocarbonic acid)



$$\begin{array}{l} \mathrm{O{-}R} \\ | \\ \mathrm{C{=}S} \\ | \\ \mathrm{S{-}H} \end{array}$$

(ester of dithiocarbonic acid)



$$\begin{array}{l} \mathrm{O{-}C_6H_9O_4} \\ | \\ \mathrm{C{=}S} \\ | \\ \mathrm{S{-}Na} \end{array}$$

(sodium salt of cellulose ester of dithiocarbonic acid, or sodium cellulose dithiocarbonate viscose)

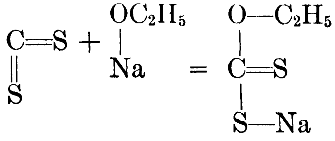
The last formula shows viscose to be the sodium salt of an ester of dithiocarbonic acid, but it is also seen that it is the sodium salt of one of the xanthogenic acids (cellulose xanthogenic acid). Since xanthogenic acid is also called xanthic acid, viscose is the sodium salt of xanthic acid, or a xanthate. Therefore a shorter name, and one most commonly used, is cellulose xanthate, but when considered as an ester it is the cellulose ester of dithiocarbonic acid.

When cellulose is converted into viscose it functions as an alcohol. Let us see how the xanthate of a simple alcohol is made; then it will be easy to extend this to xanthates of cellulose.

When alcohol is treated with solid NaOH or a strong solution of NaOH, an alcoholate is formed as shown:

$$C_2H_5OH + NaOH \rightleftarrows C_2H_5ONa + HOH$$

Even though C_2H_5ONa is easily hydrolyzed there may be a small amount in the equilibrium mixture; at least we shall assume this, and add CS_2 to the mixture. The double bonds of CS_2 remind us of the carbonyl groups of aldehyde and ketones, one important property of which is the formation of addition compounds (with alcohols to form hemiacetals). Let sodium ethylate add to CS_2, the sodium going to S and OC_2H_5 going to C:

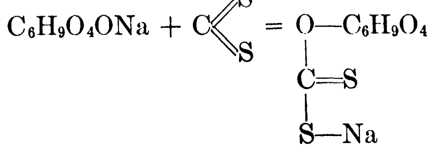


$$\begin{array}{l}\mathrm{C{=}S}\\ \| \\ \mathrm{S}\end{array} + \begin{array}{l}\mathrm{OC_2H_5}\\ | \\ \mathrm{Na}\end{array} = \begin{array}{l}\mathrm{O{-}C_2H_5}\\ | \\ \mathrm{C{=}S}\\ | \\ \mathrm{S{-}Na}\end{array}$$

This product is a xanthate of ethyl alcohol. Now let us extend this to cellulose.

There is evidence that only one of the three OH groups known to be present in each glucose unit of cellulose is xanthated, and so we shall write the formula for cellulose as $C_6H_9O_4OH$. In the Cross and Bevan method for making cellulose xanthate, loose cellulose (or sheet form cellulose) is steeped in 18% NaOH until thoroughly saturated. The material is then pressed until its weight is three times the original weight of cellulose. We can assume that we now have alkali cellulose (analogous to sodium ethylate), $C_6H_9O_4ONa$. Next, it is aged until it has the consistency of crumbs and is then treated with carbon disulfide, to form cellulose xanthate:

$$C_6H_9O_4OH + NaOH \rightleftarrows C_6H_9O_4ONa + HOH$$

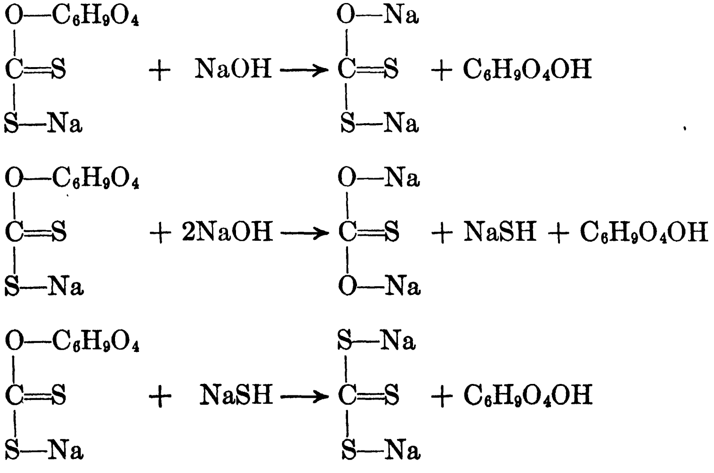


At this point the solid mass looks like deep orange-colored crumbs. This color change can be used for determining the completion of the xanthation reaction. If crumbs are broken open and the interior portions have the same deep orange color as the exterior surface, the xanthation is complete.

Cellulose xanthate made in this way is soluble in water and more soluble in dilute NaOH. If it is dissolved in dilute NaOH a thick, viscous, deep orange-colored solution called viscose is obtained. In the manufacture of rayon this solution is allowed to ripen for several days, after which it is extruded into an acid coagulating bath, which regenerates cellulose in the form of a filament.

The difference between viscose and viscose rayon should be made clear. Viscose is a thick viscous solution of the sodium salt of cellulose xanthate. Viscose rayon is regenerated cellulose made by the viscose process, or cellulose regenerated from viscose by acid coagulation.

The chemistry of the xanthation of cellulose, as described on the preceding pages, appears to be quite simple, but the facts are that it is far from simple, and the most rigid controls must be maintained if an acceptable product is to be made. The over-all equilibrium in the system is quite sensitive and susceptible to small changes of conditions. In addition, side reactions can take place, which not only disturb the equilibrium in the main reaction but also decompose the xanthate. Three such reactions are shown here.

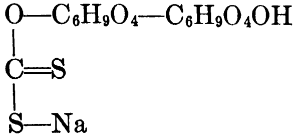


$$\begin{array}{l}O\text{—}C_6H_9O_4\\ |\\ C{=}S\\ |\\ S\text{—}Na\end{array} + NaOH \longrightarrow \begin{array}{l}O\text{—}Na\\ |\\ C{=}S\\ |\\ S\text{—}Na\end{array} + C_6H_9O_4OH$$

$$\begin{array}{l}O\text{—}C_6H_9O_4\\ |\\ C{=}S\\ |\\ S\text{—}Na\end{array} + 2NaOH \longrightarrow \begin{array}{l}O\text{—}Na\\ |\\ C{=}S\\ |\\ O\text{—}Na\end{array} + NaSH + C_6H_9O_4OH$$

$$\begin{array}{l}O\text{—}C_6H_9O_4\\ |\\ C{=}S\\ |\\ S\text{—}Na\end{array} + NaSH \longrightarrow \begin{array}{l}S\text{—}Na\\ |\\ C{=}S\\ |\\ S\text{—}Na\end{array} + C_6H_9O_4OH$$

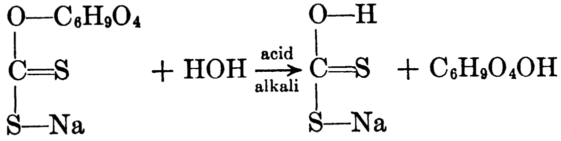
We have discussed the reaction between cellulose, NaOH, and CS_2 to make cellulose xanthate, and have seen that xanthate radicals are substituted in place of one OH group of anhydroglucose units, but nothing has been said about how general or how uniform this substitution is. Much work has been done in an effort to arrive at some conclusion about this, but some of the possibilities are still unsettled. Heuser[27] discusses this work and arrives at the following conclusion: the cellulosic substance in viscose solutions shortly after its preparation (before it is aged) has the formula shown here.



$$\begin{array}{l} O\text{—}C_6H_9O_4\text{—}C_6H_9O_4OH \\ | \\ C{=}S \\ | \\ S\text{—}Na \end{array}$$

This indicates that there is one xanthate group for every two glucose units. Furthermore, they are uniformly distributed over the chains of glucose units in cellulose. The only point that has not been proved is whether every second glucose unit throughout the system is xanthated or whether every unit of alternate chains is xanthated.

If cellulose xanthate is an ester, it should be possible to hydrolyze it, for this is a characteristic property of any ester. We know that such hydrolyses with water alone are very slow, but in the presence of either acid or alkali the hydrolysis is greatly accelerated. We also know that the hydrolysis of an ester (page 42) results in the formation of an acid and an alcohol. That is, during hydrolysis of an ester, OH groups which had been blocked (or substituted) with acid groups are liberated, and the acid group is split off. Therefore, if cellulose xanthate were subjected to any hydrolytic conditions, xanthate groups should be split off and cellulosic OH groups regenerated. A simple equation for this is



$$\begin{array}{l} O\text{—}C_6H_9O_4 \\ | \\ C{=}S \\ | \\ S\text{—}Na \end{array} + HOH \xrightarrow[\text{alkali}]{\text{acid}} \begin{array}{l} O\text{—}H \\ | \\ C{=}S \\ | \\ S\text{—}Na \end{array} + C_6H_9O_4OH$$

The monosodium dithiocarbonic acid immediately decomposes into CS_2 and NaOH.

It would seem that if viscose solutions were allowed to stand (especially in the presence of air containing carbonic acid), hydrolysis would take place and cellulose would be regenerated. However, let us think about the problem in the converse way, i.e., during such hydrolysis of viscose, xanthate groups would be split off. This is the way in which we shall want to discuss the chemical reactions that take place during the ripening of viscose. When cellulose xanthate is being manufactured for commercial use, the ripening procedure or step is perhaps the most important one, because the characteristics of the cellulose which will be regenerated after ripening are dependent upon the reactions that take place during ripening.

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[27] *The Chemistry of Cellulose*, John Wiley & Sons, 1944, pp. 333–337.

The changes that take place during ripening are rather complicated, but we can divide them into two types, changes in the colloidal nature of the solution and chemical changes which take place. Viewed from the chemical standpoint, ripening is a hydrolytic reaction that is the reverse of xanthation. During xanthation xanthate groups are put on, and during ripening they are taken off. Thus the ripening period is a time during which cellulose xanthate gradually loses its xanthate groups and approaches the composition of the original cellulose.

ACTION OF ALKALI ON CELLULOSE

Whereas cellulose is very sensitive to the action of mineral acids (even very dilute acids) and oxidizing agents, it is quite resistant to alkalies, even strong caustic alkalies at high temperature and pressure. And yet we cannot say that nothing happens when cellulose is treated with caustic alkali, because something very definite does happen. Based on such a reaction is one of the most important processes used in the textile industry, the mercerization of cotton.

It is well known that cotton fibers swell to a small extent when they are immersed in water. This is the beginning of the process of dispersion in which the structural units of cellulose are forced farther and farther apart until, at the other extreme, when cotton is treated with cuprammonium hydroxide, we say it dissolves (so completely is it dispersed that it appears to be in solution). When cellulose is treated with a 2% solution of NaOH, the swelling is slightly greater than when it is immersed in water, but not much more. The amount of swelling increases slowly as the concentration of NaOH is increased, until, when 14 to 18% NaOH solutions are used, the swelling becomes very significant and reaches a maximum value in about 23% NaOH. If the action of 18% NaOH on a single cotton fiber is observed under a microscope, a series of astonishing physical changes are seen to take place. The spiral twists of the cotton fiber uncoil until all of the convolutions disappear. At the same time, the fiber shrinks and becomes thicker. A cross-section microphotograph of the fiber would show that the lumen (central canal) has contracted until it is almost a point. When these changes are extended to the behavior of cotton yarn or cloth, we encounter results of unusual importance. These are discussed in Chapter 7.

There has been a great amount of speculation, resulting from a large number of studies, as to whether a real chemical compound is formed when NaOH acts upon cellulose. There is no doubt that cellulose takes NaOH out of solution and absorbs it preferentially, and there are three possible types of product that might result from such removal of NaOH. The product may be (*a*) a real chemical compound formed by a chemical reaction, with definite proportions of cellulose and NaOH; (*b*) an addition compound, in which NaOH molecules are added to cellulose in definite amounts; (*c*) a substance in which NaOH is merely absorbed by cellulose. It is beyond the scope of this book to go into all the pros and cons of this argument, but a few brief statements may be made about it. The first possibility can probably be ruled out because an alcoholate is almost 100% hydrolyzed by water, and so a compound such as $C_6H_7O_2(ONa)_3$ could not exist in the presence of water. (However, it is known that hydrogen gas is evolved when cellulose is added to sodium dissolved in liquid ammonia. This is like the action of sodium on alcohol which evolves hydrogen and forms an alcoholate.) As to the second and third possibilities, opinions differ greatly. One group of workers thinks that a definite addition compound is formed, and the consensus of opinion is that this compound has the formula $(C_6H_{10}O_5)_2NaOH$. That is, cellulose in 16 to 18% NaOH adds on 1 NaOH for each 2 glucose units. The other group of investigators, using different experimental techniques, claims that the product is only an absorption compound with no definite molar proportions.[28]

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[28] Complete reviews of the evidence on both sides may be found in Marsh's *Mercerizing*, D. Van Nostrand Company, 1942, Chapter 16, and in Heuser's *Chemistry of Cellulose*, John Wiley & Sons, 1944, pp. 65–92.

If alkali cellulose or soda cellulose, produced by the action of strong alkali on cellulose, is washed with large amounts of water, a product is obtained that is the same as native cellulose chemically, but is quite different physically. These new properties are (1) increased strength, (2) increased luster under certain conditions, (3) increased absorption of water, (4) increased absorption of certain dyes, NaOH, and iodine, and (5) increased solubility in cuprammonium hydroxide. These properties are discussed in detail in Chapter 7.

QUESTIONS

1. Write the structural formula for the anhydroglucose unit of cellulose. Show how two such units are joined together in cellulose.
2. Using the pyranose ring structure of glucose, explain how glucose can have reducing properties (an aldehyde group).
3. Discuss the arrangement of molecules in a cellulosic substance like the cotton fiber.
4. Discuss the copper number—definition, determination, uses, reason for variation in it, etc.
5. What is the most important solvent for cellulose? Give two names for it. What use is made of such solutions in cellulose and cotton chemistry? in rayon manufacture?
6. Discuss hydrocellulose—formation, composition, properties, tests for, and objections to it in textiles.
7. Discuss oxycellulose, covering the same points as in question 6.
8. At what points in the anhydroglucose unit might oxidation take place? What are the products of each?
9. How is cellulose oxidized by periodic acid and by nitrogen tetroxide?
10. What is the difference between an oxycellulose with a high carboxyl content and one with a high aldehyde content?
11. What is the connection between the *p*H of the oxidizing bath and the copper number and methylene blue number of the oxycellulose formed?
12. At what *p*H does oxidation take place most rapidly?
13. Name three important classes of compounds that are esters of cellulose.
14. How is cellulose nitrate made?
15. How is cellulose acetate made? Is it a pure chemical compound or a mixture?
16. Why is it better to have cotton swollen before it is acetylated?
17. Calculate the per cent acetic acid in the diacetate of cellulose; in the triacetate of cellulose.
18. What three kinds of substances are necessary for the acetylation of cellulose? Give an example of each.
19. What measurement is used to show that cellulose (cotton) has been degraded?
20. Which would acylate more rapidly, cotton with 2% moisture or cotton with 10% moisture?

21. What is accomplished by the technique covered by the Miles patents? What is the advantage?

22. Name some uses for cellulose acetate.

23. How is cellulose xanthate made? How is it used? What happens when a solution of viscose is acidified?

24. What two physical changes are seen when cotton fibers are immersed in 15% NaOH?

25. What are the properties of cellulose after treatment with alkali of mercerizing strength?

7 • Cotton

Cotton is one of the oldest fibers used for textile purposes. Wool was used in cold northern countries in almost prehistoric times, but in the tropical countries cotton was the important textile fiber. From about 1500 B.C. to 1500 A.D., India was the center of the world's cotton industry, and the writings of early explorers are filled with exaggerated descriptions of the fine cotton fabrics made in India. Cotton was introduced into Japan and China from India as early as 800 A.D., but extensive cultivation and use of cotton in these countries did not begin until about the thirteenth century. Cotton manufacture in England became prominent about 1635, although cotton goods had been imported much earlier than that. Cotton was being cultivated and used for clothing in America at the time of its discovery by Columbus, but the first organized cultivation by whites was begun by Virginia colonists in 1621. For the next 150 years cotton cloth in this country was homespun, but in 1787 a mill was built in Beverly, Mass., where cotton cloth was manufactured.

Although cotton is cultivated in almost every country in the world having a mild climate, the production in the United States is so large that American cotton dominates the world market, and the cotton exchanges in this country set the price of cotton. Other countries that are large producers of cotton are Egypt, India, and China.

The cotton plant (or shrub) belongs to the family Gossypium, and the varieties of cotton are different species of this family, e.g., ordinary American upland cotton is *Gossypium hirsutum;* Indian cotton is *G. herbaceum*; and sea island, Egyptian, and Peruvian cottons are *G. barbadense.* The cotton plant grows to a height of 3 to 6 feet, with flowers which develop into capsules about the size of a walnut. These capsules contain four to eight seeds, from the epidermis of which two kinds of fibers are appended.[1] The two kinds of fibers are known as lint fiber (the longer type used for spinning) and linters (the shorter type used for stuffing and for commercial manufacture into products such as rayon and explosives). Lint fibers begin to grow on the day of flowering, and linters about 10 days later. Incipient growth is recognized by a slight swelling or bulging of the cells in the seed coat. After this, a slow elongation begins which lasts for 15 to 20 days after flowering. During the elongation period, the cotton fiber consists of a hollow tube with a thin shell or wall of primary cellulose; this tube is enclosed in a protective sack or cuticle that contains the natural fats and waxes. At the end of the elongation period, the tube closes at the tip, after which lint fibers begin to deposit an inner wall (the secondary wall). This inner wall is thickened by layer after layer of cellulose, one layer each day for about 25 days. This decreases the size of the lumen (central canal running lengthwise of the fiber) until it becomes very small. During growth the fibers are cylindrical, but when they reach maturity (ripen) they collapse and form a flat, ribbon-like fiber with a spiral twist (convolutions) in it. These twists constitute an important factor in the spinning quality of the cotton. If the interior layers of cotton do not develop properly and are incompletely formed during growth, the fiber will appear as a thin-walled ribbon with no twist. This so-called dead cotton is undesirable because of its poor spinning quality and its resistance to dyes.

Cotton linters is often thought of as very short staple fibers formed by the breaking of lint fibers during ginning, but this is not correct. It is true that much of the fiber in commercial linters has been formed in this way, but the true linters is the fuzz on the seed and has a morphology of its own. Linters fibers are darker, coarser, and shorter than lint fibers. They are rarely longer than ⅛ inch and are about 20 microns in diameter. They are more cylindrical than lint fibers and have thinner walls.

After the cotton has ripened, the seeds, with their covering of fibers, are put through a cotton gin, which separates the longer lint fibers and leaves the seed covered with linters; the linters is removed by a different procedure. The lint fibers are pressed into bales for sale and transportation to mills. Production of cotton in the United States runs into millions of such bales each year. An American bale weighs 500 lb, whereas the Egyptian bale weighs 750 lb and the East Indian bale weighs 400 lb.

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[1] Hock, *Textile Research J.*, **17**, 423 (1947).

The fine structure of cotton fiber shows that the inner layers of cellulose consist of fibrils highly oriented (arranged) in a spiral fashion around the axis of the fiber, and the micelles of cellulose are arranged parallel to the fibrils. The fibrils are cemented together by an amorphous substance (unoriented). Three of the most important properties of cotton, on which its use as a textile fiber are based, are due to this fine structure. The high orientation of molecules in the fibrils leads to a good longitudinal strength; the spiral arrangement permits some elastic elongation; the amorphous cement allows the fibrils to move slightly in relation to each other during bending and, therefore, leads to a good reversible bending strength.

We have already named a botanical classification by which cotton is divided into three varieties. There are others, but they are of minor importance compared with these three. Each of these botanical varieties can be subdivided into commercial varieties based on various factors. For example, the *G. barbadense* is cultivated in Egypt, Peru, the West Indies, and islands off the southern Atlantic coast. It is reasonable to think that the qualities and properties of cottons grown in such widely separated parts of the world might vary somewhat, even though they belong to the same botanical specie. Differences in soil, climate, elevation of land, method of cultivation, etc., would account for differences in cotton. If cotton is to be used for making yarn and cloth or knit goods, the dimensional characteristics of the fiber are perhaps the most important property to be considered.

There are long, medium, and short staple cottons, and fine, medium, and coarse cottons. If yarns are to be spun and used for some particular purpose, a careful selection of fiber must be made. If smooth, uniform yarns are wanted, fine and coarse fibers must not be mixed. If the tensile strength of yarns is to be especially important, short fibers must not be mixed with long fibers. Such things are so important that cotton is often graded as to length in increments of $\frac{1}{16}$ inch. Tables 22 and 23 contain figures selected from various sources to show the dimensional characteristics of several of the better-known cottons. In Table 22 the commercial varieties have been arranged in decreasing order of their mean lengths. The second column shows the usual minimum and maximum lengths. The third column shows the mean width of the fibers, and the last column gives the counts of cotton yarns (see page 100) made from these fibers. All dimensional figures are in inches. Table 23 shows the mean total cross-section areas of a few cotton varieties. These figures probably emphasize the difference between fine and coarse cottons better than the figures for mean width. When one kind of cotton has a cross-section area two or three times greater than another kind, the difference between yarns made from two such types can be visualized.

TABLE 22

DIMENSIONAL CHARACTERISTIC OF COTTON FIBERS

Variety of Cotton	Length Variations, in.	Mean Width, in.	Count of Yarn
Pima (American)	1.52–1.87	.00065	180–250
Florida sea island	1.50–1.81	.00064	150–200
Peruvian sea island	1.37–1.75	.00067	80–140
Sakel (Egyptian)	1.40–1.70	.00065	80–150
Brown Egyptian	1.12–1.50	.00074	50–90
Smooth Peruvian	1.12–1.44	.00077	40–70
White Egyptian	1.12–1.37	.00077	40–70
Pernambuco (Brazilian)	1.12–1.37	.00079	40–60
American Egyptian	1.12–1.37	.00064	50–60
American peelers	1.12–1.37	.00077	40–60
Orleans (American)	0.94–1.12	.00076	30–50
Fine American upland	0.90–1.10	.00067	50–90
Coarse American upland	0.90–1.10	.00075	30–50
Mobile (American)	0.75–1.00	.00076	to 36
Indian	0.70–1.00	.00083	to 30

TABLE 23

CROSS-SECTIONAL FEATURES OF COTTON FIBERS

(Total area including lumen)

Very fine sea island	0.0039 sq in.
Fine American upland	0.0061 sq in.
Coarse American upland	0.0091 sq in.
Coarse Asiatic	0.0147 sq in.

Another physical characteristic of cotton fibers which has much to do with their spinning quality is the amount of spiral twist in the fibers. Cotton fibers are quite short compared with other textile fibers, and yet they can be spun into yarns which have sufficient strength to make fabrics that wear well and give long service. The twist in the individual fibers is responsible for much of this, because it helps the fibers to cling together when they are spun. The number of twists per inch in cotton fibers reported in the literature is quite confusing. However, we can make some general statements about it. The number of twists per inch runs from 150 to 300, and the arrangement of cottons in order of the decreasing number of twists is Pima, sea island, Egyptian, Brazilian, American, and Indian.

PHYSICAL PROPERTIES OF COTTON

The cotton fiber is a long single cell closed at one end. It resembles a collapsed tube which was twisted as it collapsed, so that it has the appearance of a narrow flat ribbon with spiral twists. A central canal, the lumen, runs through the fiber, and in the cross-section of ripe cotton it looks like a thin irregular loop. In dead cotton, the lumen is practically absent. Such fibers are of low quality because they are weak and brittle, have poor spinning quality, and resist dyes so that they show up as undyed specks in colored goods.

Cotton is affected by heat at about 150° C, but the effect is not noticeable unless the heat is maintained for a long time. In such instances the copper number increases and the viscosity decreases. At about 170° C cotton begins to scorch even in a short time. If cotton is distilled out of contact with air, it chars and decomposes to yield small amounts of gaseous products, alcohol, and acetic acid. At high temperatures in air, cotton burns freely, leaving no bead.

It is well known that cotton will absorb moisture from the air and still feel dry. This is characteristic of all substances having large surfaces. If cotton is dried at 110° C, it loses weight because of the loss of moisture, but when exposed to air the moisture will be regained. The amount of moisture in cotton depends on two things, the relative humidity and temperature of the air to which it is exposed. The relative humidity is more important than the temperature; that is, cotton will retain a constant moisture content over narrow ranges of temperature, but small changes in humidity affect the moisture content significantly. The moisture content of cotton conditioned at 70° F but at different humidities is shown in Table 24.

The variation in moisture content of cotton conditioned at a constant humidity but at different temperatures is shown in Table 25.

TABLE 24

RELATION BETWEEN HUMIDITY AND MOISTURE CONTENT OF COTTON

Relative Humidity, %	Moisture, %, at 70° F
40	5.65
50	6.63
60	7.69
70	8.79
80	10.23
90	11.85

Absorption of water by cotton affects some of its physical properties, the most important of which are strength and elongation. Peirce and Stephenson[2] worked with single yarns of various counts and determined the strength (grams required to break the yarns) and elongation at the break, in atmospheres of different relative humidities. The figures shown in Table 26 are averages of 100 tests after conditioning the yarns at the specified humidities. The original length of each yarn was 20 in. Two additional columns have been included to show the percentage increase in the values as compared with the dry yarns.

TABLE 25

RELATION BETWEEN TEMPERATURE AND MOISTURE CONTENT OF COTTON AT 70% RELATIVE HUMIDITY

Temperature, ° F	Moisture, %, at 70° R.H.
50	9.14
60	9.00
70	8.79
80	8.58
90	8.32
100	8.05

The figures in Table 26 show that cotton yarns become increasingly stronger as the moisture content increases, until they are more than one-third stronger. At the same time the elongation increases even more rapidly, so that in atmospheres above about 80% R.H. it has increased 60%. It must be understood that these relationships hold true only for native undegraded cotton. If cotton is degraded by any process or treatment, its wet strength is less than its dry strength.

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[2] *J. Textile Inst.*, **17**, T645 (1926).

When cotton absorbs large amounts of water or is in contact with water, it shows a decided swelling, and we shall find later in this chapter that this is one of the most important factors in the shrinkage of cotton goods.

TABLE 26

Effect of Humidity on Strength and Elongation of Single Cotton Yarns (50's)

Relative Humidity	Strength, gm	Increase in Strength, %	Elongation, mm	Increase in Elongation, %
0	160.0	....	22.0	....
30	186.1	16.3	22.9	4.1
50	195.3	22.1	28.7	30.5
70	207.4	29.6	30.7	39.6
85	213.9	33.7	35.4	60.9
92	217.3	35.8	35.3	60.5
100	217.6	36.0	34.5	56.8

It is thought that water absorption may be both physical and chemical. Physically absorbed water (moisture) can be removed by heating cotton for a period of time, but there is still water in the yarn or cloth which requires more radical treatment for its removal. Even a high vacuum and temperature may be necessary. This leads us to think that this tightly held water may be chemically bound to the OH groups of cellulose by some sort of hydrogen bond type of linkage. This idea is supported by the fact that cellulose nitrates or acetates (in which part of the OH groups are blocked by substitution) absorb considerably less water than native cotton. On the other hand, mercerized cotton absorbs more moisture. This is probably due to the swollen condition of mercerized cotton which means more surface exposure. Other observations support this conclusion. If cotton is exposed to high humidities at increasing temperatures, there is a rapid increase in the amount of water absorbed when 60° C is reached.

This is probably due to the swelling of cotton under these conditions, thereby exposing more surface which will absorb more water.

When moisture determinations are made in the laboratory, samples of cotton are heated in an oven at 105° C for 24 hours. This accomplishes the same thing as drying in a desiccator over P_2O_5 for several days.

CHEMICAL COMPOSITION OF COTTON

Native cotton is the purest form of natural cellulose and is not combined with lignins or pectins, as is the cellulose of flax, jute, hemp, wood, etc. Like all vegetable tissues, it contains a certain small amount of mineral matter which is left as an ash after cotton is burned. The amount of ash is about 1–1.5%, and if it is found to be much greater than that, it is considered to be mechanically attached dirt. When cotton is carefully cleaned, the amount of ash drops to about 0.1%. The mineral matter in cotton consists of chlorides, carbonates, and phosphates of potassium, calcium, and magnesium. Coloring matter in cotton varies so much that no general statement can be made about it. American cotton is quite white, but some Egyptian and Peruvian cottons are brown and brownish red. A small amount of vegetable protein is found in cotton, a little over 1%. The impurity found in the largest amount consists of pectinous materials. These are removed by boiling alkali when cotton is prepared for bleaching. A small amount of fatty material, which is mostly cottonseed oil, is found in raw cotton. It probably comes from cotton seeds which are slightly damaged during ginning. Raw cotton contains about 0.5% of a waxy substance which seems to serve as a protective coating on the surface of the fiber. Cotton wax is insoluble in water, and because of this, raw cotton is very hard to wet. It is well known that unbleached cotton will not soak up water as easily as bleached cotton. This wax is another impurity that is removed by the alkali boil which precedes bleaching. After cotton is purified, all of these impurities are reduced to a total of about 1%.

There are several factors that influence the chemical analysis of raw cotton, but the following figures give a general idea of a sort of average analysis. If the impurities are calculated on an oven-dry basis, the percentage of fiber would be 89.76%, and after careful purification it would run close to 99%.

Ash	1.65%
Protein	1.50
Nitrogen-free extract	5.79
Fat	0.61
Fiber	83.71
Water	6.74

Chemical Properties of Cotton

ACTION OF COTTON WITH ACIDS

Cotton is quite sensitive to the action of dilute mineral acids, but is very little affected by organic acids (some of which are used with little danger as sours in laundering operations). The chemical reaction that takes place is one of hydrolysis, with the formation of a series of hydrocelluloses (page 134) in which cotton is increasingly modified. When cotton is treated with dilute mineral acids, it loses some weight and some strength, gradually becomes brittle, and finally breaks up into a fine powder. We are interested only in the early stages of acid attack, when the cloth or yarn still retains its fibrous form. After this is lost, it is no longer a textile problem.

The point of attack on cotton cloth is at the surface, where glycosidic linkages are broken and reducing groups are formed simultaneously. The action of acid progresses inward from the surface, but at a slower rate because the points of attack are less accessible. Part of these products are soluble in hot alkali, and a partially hydrolyzed cloth will lose weight if it is boiled with NaOH. We may use this alkali solubility to follow the progress of the reaction.

Since reducing groups are formed by the action of acid on cotton, the course of the reaction may also be followed by means of copper number determinations (page 135). Another criterion of the course of hydrolysis is the viscosity of cuprammonium solutions of the cotton. The viscosity of such solutions is a measure of the average chain length of the high-polymeric cellulose molecules, and so, if chains are ruptured by acid attack, the average length will decrease and the viscosity drop to lower values.

If we are to study the effect of acids on cotton and be impressed by the necessity for extra care in all operations in which cotton may come into contact with acids, we must first find out how sensitive cotton is to acids. We must answer the question, How small an amount of acid will cause a modification of cotton?

After that we shall want to know how the extent of acid attack varies with such factors as time and temperature.

Cohen[3] determined the smallest concentration of HCl and H_2SO_4 which would show a measurable effect when cotton is boiled in the acids for one hour and then dried at different temperatures. Copper numbers and tensile strength were used to test the yarn. Some of the results are shown in the following list. The concentration of the two acids are expressed in grams per liter. These concentrations are the smallest that will show a change in copper number and a reduction in tensile strength.

HCl 0.08 gm/l (0.002 N) dried at 25° C
H_2SO_4 0.30 gm/l (0.006 N) dried at 25° C
HCl 0.025 gm/l (0.0007 N) dried at 100° C
H_2SO_4 0.08 gm/l (0.0016 N) dried at 100° C

The surprising thing about these results is that HCl attacks cotton more easily than does H_2SO_4, and therefore would damage cotton more readily. This will also be found true in some other work to be quoted later. These two acids in solutions stronger than those listed will always hydrolyze cotton.

If the effect of the action of dilute mineral acids on cotton is a cumulative one, the products obtained by longer action should be more degraded and modified. A brilliant and thorough investigation of this whole subject was made by Birtwell, Clibbens, and Geake,[4] in which the acid treatments were such that only a small amount of hydrolysis took place and the visible appearance of the cloth was unchanged. The work is too extensive to review in this book, but it is recommended to any reader who wants a complete discussion of the subject of the mild acid hydrolysis of cotton.

More recently Davidson[5] extended the investigations of Birtwell, Clibbens, and Geake by using stronger solutions of acids. The course of the hydrolysis was followed by determining the loss in weight suffered by the cotton, and the cuprammonium viscosity and alkali solubility of the hydrocellulose formed when cotton was immersed in acids of different strengths at different temperatures.

In each instance there was a rapid increase in fluidity in the first few hours of acid treatment, after which the change was much slower and the fluidity leveled off to a constant value. The solubility in alkali showed the same behavior. One of the most interesting things brought out by the investigation was the fact that HCl affects cotton much more than H_2SO_4. This is shown in Table 27, where some of Davidson's results are given. Both acids reach about the same maximum effect as measured by fluidity and alkali solubility, but the HCl reaches it much sooner than H_2SO_4. The fluidity of HCl hydrocellulose reaches its maximum after about 40 hours acid treatment, whereas H_2SO_4 hydrocellulose requires about 300 hours. The maximum solubility of HCl hydrocellulose is reached after about 100 hours, but with H_2SO_4 hydrocellulose, about 500 hours are required.

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[3] *J. Soc. Dyers Colourists*, 162 (1915).

[4] *J. Textile Inst.*, **17**, T145 (1926).

[5] *J. Textile Inst.*, **34**, T87 (1943).

TABLE 27

ACTION OF ACIDS ON COTTON

(20° C)

Time, hours	Loss in Weight by Cotton, %		Fluidity		Loss in Weight in Alkali, %	
	10 *N* HCl	10 *N* H_2SO_4	10 *N* HCl	10 *N* H_2SO_4	10 *N* HCl	10 *N* H_2SO_4
0			5.6	5.6	1.0	1.0
1			32.0		14.3	
2			36.2		22.3	
4	0.9		42.6	16.9	31.1	4.9
8				20.5		6.5
9	1.9		46.7		39.9	
16	3.3		48.0	26.7	45.8	9.8
48	6.6		49.1	36.0	47.1	18.8
120	8.95	0.4	49.4	41.8	49.9	29.2
240	10.15		49.5		50.2	
288		0.5		46.5		39.2
432				47.1		42.8
576				47.8		44.7

Supposing that a cotton cloth has been damaged by acid hydrolysis over a particular area and begins to break and split in this area, what is the chemical picture of the cloth and what are its properties (some of which may be used to test for hydrocellulose)? If the cloth has been damaged that amount, there will be a considerable accumulation of hydrolysis products on the surface, and hydrolysis will have progressed inward to quite an extent. If the cloth is boiled in NaOH, some of the surface layer will dissolve and the cloth will lose weight. If the cloth (before boiling with alkali) is boiled with Fehling's solution or a modified Fehling's solution, it will be found to have a large copper number (5 or higher), but after boiling with NaOH the copper number will be about the same as for ordinary clean cotton. If this test is made in a qualitative way, the hydrolyzed area will be colored reddish brown; the cloth will be yellowed by hot alkali; it will absorb methylene blue to a small extent if the damage has been caused by submerging the cloth in acid solution. However, if the cloth has been in an acid solution and then removed and ironed while acid is still present, the methylene blue absorption will be high, and the hydrolyzed area will be more sensitive to heat and will scorch with a hot iron sooner than undamaged areas.

What has been said up to this point refers to the action of dilute mineral acids on cotton, but what about the effect of stronger acids? One might think that, if it is possible to damage cotton with dilute acids, concentrated acids would damage it beyond repair. However, we shall find that strong H_2SO_4 and HNO_3 can be employed for making useful products from cotton cellulose.

In the well-known method for parchmentizing paper, strong H_2SO_4 is used. Paper is passed through a solution of H_2SO_4 of about 78% (sp gr = 1.71) at 10° C at such a rate that it is in contact with the acid for about 15 seconds, and is passed into a large amount of water, then washed thoroughly, and dried. The surface of the paper seems to be peptized by the strong acid, and when the paper is passed into water the cellulose is regenerated on the surface. This fills up the pores of the paper and gives to it the well-known parchment appearance and handle. It is then quite water- and oil-repellent and is much stronger and semitransparent. Paper to be parchmentized by this method must be very free from lignin in order to avoid the formation of a pronounced brown discoloration. Sulfuric acid solution of 70% may also be used, in which case the reaction is not quite so rapid but is more easily controlled.

ACTION OF COTTON WITH OXIDIZING AGENTS: BLEACHING

The student of textile chemistry should be interested in the oxidation of cellulose because it is one of the principal causes of trouble, dissatisfaction, and complaint in the use, wear, and life of cotton and linen fabrics. A great amount of research has been done on cellulose oxidation from the purely scientific standpoint, using all types of oxidizing agents under various conditions and examining the products in different ways. In a large proportion of this research, the oxidation has been carried to the extreme by completely decomposing the cellulose. We discussed much of this work in Chapter 6. Although such results are of academic interest to the textile chemist, he is much more interested in the very earliest stages of oxidation that occur during the bleaching of cotton, as it is to this that he can trace many of the faults which later develop in the goods.

Obviously, cotton is bleached to make it whiter, but this must be accomplished with a minimum of damage to the cotton itself. This is not easy, because the coloring matter is destroyed by means of oxidation, and as cotton is also attacked by the same reaction, it is difficult to bleach the coloring matter and at the same time to avoid oxidizing some of the cotton. The textile chemist is, therefore, very much interested in the oxidation of cellulose and in the properties of the products of such a reaction. As the oxidation of cellulose is so vitally associated with the important operation of the bleaching of cotton, we shall make a brief study of bleaching before taking up the oxidation itself.

The bleaching agent almost universally used on cotton is a hypochlorite of some sort, and of these only two are of any commercial importance, namely calcium and sodium hypochlorites. Bleaching powder, chloride of lime, is made by passing chlorine gas over wet lime:

$$Ca(OH)_2 + Cl_2 \longrightarrow Ca(OCl)Cl + HOH$$

It is quite hygroscopic, and deteriorates if exposed to air. When it takes up atmospheric moisture or is treated with water, a molecular change takes place as follows:

$$2Ca(OCl)Cl \longrightarrow Ca(OCl)_2 + CaCl_2$$

In order to stabilize bleaching powder for shipment, an excess of lime is left in it. Slaked lime is not very soluble in water, so that when bleaching powder is stirred with water, part of it dissolves and a sludge of lime is left on the bottom. Thus the clear solution will contain a mixture of calcium chloride and calcium hypochlorite, and will be saturated with calcium hydroxide. For use in bleaching, this clear liquor is drawn off and diluted the proper amount. The alkalinity of the solution (due to the hydroxide) is an important factor in the stability of the bleach liquor.

Sodium hypochlorite may be used in place of calcium hypochlorite. This bleach can be made in three general ways: (1) The addition of Na_2CO_3 to $Ca(OCl)_2$ solutions

$$Ca(OCl)_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaOCl$$

will precipitate $CaCO_3$, and the supernatant solution of NaOCl may be drawn off and diluted to the proper strength. (2) Chlorine gas may be passed into NaOH

$$2NaOH + Cl_2 \longrightarrow NaOCl + NaCl + HOH$$

(3) In the preparation of electrolytic bleach, an electric current is passed through a solution of ordinary salt. At the negative electrode, sodium ions are changed to sodium atoms, which immediately react with water to form NaOH. At the positive electrode, Cl_2 is liberated. The mixture of NaOH and Cl_2 produces NaOCl.

Since bleaching is an oxidation reaction, we must consider what the real oxidizing agent is. Both NaOCl and $Ca(OCl)_2$ are hydrolyzed to a small extent in solution to form small amounts of hypochlorous acid, HOCl. Chlorine water is also a bleaching agent, although a weak one, and it is known that it is in an equilibrium mixture, as shown by the following equation:

$$Cl_2 + HOH \rightleftarrows HOCl + H^+ + Cl^-$$

It has been demonstrated that bleaching action is not due to undissociated molecules of sodium or calcium hypochlorite, nor to the hypochlorite ion. Since all the previously mentioned bleaching agents yield hypochlorous acid in solution, it might seem that HOCl does the bleaching, but the real oxidizing agent is the oxygen from the HOCl.

$$HOCl \longrightarrow O + HCl$$

Since this oxygen comes from the undissociated molecules of HOCl, it is apparent that HOCl is the potential source of bleaching action, and any condition that favors the formation of HOCl molecules will increase bleaching efficiency.

The stability of bleach liquor is the converse of its bleaching efficiency. If it is to function as a bleaching agent, it must decompose to give HOCl, which in turn yields oxygen. Thus, the more stable a bleach liquor is, the less readily it will decompose and hence the less bleaching it can do. During the time that bleaching powder or a stock solution of it is stored, it is desirable that the amount of decomposition be kept at a minimum, but when a dilute solution is being used for bleaching, we want its stability decreased so that it will bleach in a short time. In other words, we should like some way to control the rate of bleaching.

Alkali will react with HOCl and convert it into a hypochlorite. Remember that the hypochlorite ion is not responsible for bleaching action; the hypochlorous acid itself is the agent. Therefore if the acid is neutralized, it cannot decompose. Bleach liquor may also be stabilized by storing it as a strong solution. Dilute solutions will decompose much faster than strong solutions.

The rate of bleaching may be controlled in various ways. We have found that high alkalinity stabilizes the bleach and lowers the rate of bleaching. The opposite condition, acidity, should increase the rate of bleaching, unless the acidity is too great (excess of HCl will form chlorine water and not HOCl). If acidity and alkalinity are so closely connected with rate of bleaching, some control of the *p*H of the bleach bath should regulate the rate of bleaching. Commercial bleaching is done in baths where the *p*H range is from 5 to 9, and within this range maximum bleaching efficiency is obtained. But reference to page 146 will show that this is also the range in which the cotton itself will be most easily oxidized and damaged. Most damage is done to cotton in a neutral hypochlorite bath ($p\text{H} = 7$), so that the bleacher sees to it that his bath has a *p*H either above or below 7. Both heat and sunlight will increase the rate of bleaching.

If the *p*H of bleach liquor seems to be so important, it is interesting to get some mathematical expression that will show the relation between the concentration of H^+ ion, OCl^- ion, and HOCl molecules in a bleach liquor. This will be determined by the ionization constant

$$\frac{[H^+][OCl^-]}{[HOCl]} = K_a$$

of HOCl. Davidson[6] found the value of K_a to be 3.7×10^{-8}. This means that HOCl is a much weaker acid than acetic acid, and also that the equilibrium is quite sensitive to small changes in $[H^+]$.

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[6] *J. Textile Inst.,* **24,** T185 (1933).

If bleach baths are acidified with HCl, some chlorine will be formed according to the chlorine water equilibrium shown on page 177. The equilibrium constant for this system is shown here.

$$\frac{[H^+]\,[Cl^-]\,\overline{[HOCl]}}{[Cl_2]} = K_{eq}$$

Viviani[7] found this value to be 3.5×10^{-4}. Davidson[8] studied the hypochlorite bleaching of cotton under controlled conditions and found that below a *p*H of 6 chlorination is probably taking place; that above a *p*H of 8 oxidation is taking place; and that between the two both reactions are going on.

Control of *p*H has been mentioned. This means not only starting with a liquor of proper *p*H but also controlling it during the time of bleaching. Soon after bleaching begins, the strength of the bleach liquor decreases rapidly, and the *p*H starts to go down (it may start at 11, drop to the neutral point, and go on into the acid range of 6 or 5). Davidson[9] showed in one instance that the grams per liter of available chlorine dropped from 4.8 to 2.6 in 30 minutes, and the *p*H changed from 11.0 to 8.4 in the same time. Davidson, in his paper, shows the types and amounts of various buffers that can be used to maintain a constant *p*H during bleaching.

Recall that cotton is sensitive to dilute mineral acids as well as oxidizing agents, and then note that when HOCl furnishes oxygen for bleaching, the other product is HCl. It is true that HCl is formed in only small amounts in this way, but it will be in contact with cotton for several hours, and, in local areas where circulation is poor, acid hydrolysis may occur.

Some bleachers will remove cotton goods from the bath before the bleaching is completed, and hang them in air. Let us see what is gained by such a procedure. Air contains CO_2, which in the presence of water behaves like a weak acid, H_2CO_3. Carbonic acid will slowly react with calcium hypochlorite left in the goods:

$$Ca(OCl)_2 + H_2CO_3 \longrightarrow 2HOCl + \underline{CaCO_3}$$

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[7] *Ind. Eng. Chem.*, **33**, 741 (1941).

[8] *J. Textile Inst.*, **33**, T33 (1942).

[9] *J. Textile Inst.*, **33**, T33 (1942).

Calcium carbonate, because of its insolubility, will be deposited on the goods or remain suspended in the small volume of liquor distributed through the goods. Now suppose that the HOCl decomposes and furnishes oxygen to complete the bleaching. At the same time HCl will be formed, but it will react with $CaCO_3$ and, therefore, have no chance for hydrolyzing the cotton. The completion of a bleaching operation by exposure to air seems to be a safe and sensible thing to do.

The strength of hypochlorite bleach liquors is expressed in terms of available chlorine. This is rather confusing when it is oxygen, and not chlorine, that does the bleaching. However, if we know the available chlorine, we know that a certain amount of oxygen is equivalent to it. If NaOCl solution is treated with KI and acidified, the reaction is

$$NaOCl + 2HI \longrightarrow NaCl + H_2O + I_2$$

The liberation of two iodine atoms by one molecule of NaOCl is the equivalent of one atom of oxygen. However, note that there is only one chlorine atom in NaOCl. We know one oxygen is equivalent to two chlorines, and so NaOCl when judged as an oxidizing agent is equivalent to two chlorines, even though it contains only one chlorine. Therefore, when bleaching powder is analyzed and the result is expressed in terms of percentage of available chlorine, it means that the oxidizing power is equivalent to that much chlorine, but only half that amount of chlorine is actually present as hypochlorite.

Look at it in a different way. When chlorine is passed into NaOH,

$$2NaOH + Cl_2 \longrightarrow NaOCl + NaCl + H_2O$$

only half the chlorine is in the hypochlorite, but the oxidizing power of the hypochlorite is equal to the entire amount of chlorine.

In commercial practice the strength of bleach liquors may be checked by specific gravity. They are made up to be from 1° Tw to 2.5° Tw, which corresponds to 2.7 to 7.0 gm Cl per liter. The amount of ordinary bleaching powder required for one gallon of such bleach runs from 1.2 oz to 3.2 oz.

BOILING OUT COTTON

Raw unbleached cotton contains very few impurities, but those few are nuisances. The thin coating of wax makes cotton quite water-repellent, and it must be removed before good bleaching can be done. The pectinous impurities tend to form gels under certain circumstances, and they must also be removed. The small amount of fatty impurity must also be eliminated. All of this is accomplished by the so-called boiling out of unbleached cotton. There are two general methods for boiling out, the lime method and the soda method.

The *lime boil* consists of three steps: the lime boil, the gray sour, and the soda ash boil. In the first and last steps, a kier is used. This is similar to an autoclave with a cylindrical inner chamber with perforated walls. Means for heating must be provided, as well as some sort of efficient circulating system by which liquid can be pumped through the goods that are packed in the inner chamber. The cloth is saturated with milk of lime so that it takes up about 5% of its weight of lime. It is then packed into the kier very carefully, so that no air pockets are present, and covered with more suspension of lime. The total lime should be 8 to 12% of the weight of the goods. The lid is clamped on and the cotton is boiled, or rather, boiling limewater is circulated through it, for 8 to 12 hours. During this operation, nitrogenous impurities are converted into ammonium salts, and fats and waxes are saponified. As the alkali used for this saponification is $Ca(OH)_2$, the resulting soap will be a calcium soap. At the end of this boiling period, the limewater is drawn off and cold water is run in at the same time. Care must be used to prevent the goods from coming into contact with hot iron while still saturated with lime. This would cause what is known as lime burns and would weaken the cloth.

The goods, after this washing, are transferred to a solution of HCl or H_2SO_4 (sp gr $= 1.005$ to 1.01). This is known as the gray sour, because the goods at this time are really darker in color than they were at the beginning. The acid treatment removes mineral salts such as carbonates, but its more important function is to change calcium soaps to free fatty acids. The gray sour should be cold, because cotton is sensitive to dilute mineral acids. For the same reason the goods should not be left in the acid too long, but should be washed well and passed to the next operation.

For the soda ash boil the goods, packed in a kier, are boiled for 8 to 12 hours with a solution of soda ash. This converts the insoluble fatty acids (liberated in the gray sour) into sodium soaps.

The goods are then thoroughly washed. The cotton is now free from all impurities except the coloring matter, which will be destroyed during bleaching.

The *soda boil* is a much shorter and simpler method for preparing cotton for bleaching, and it is being more generally used than the older lime boil. When cotton is prepared by this method, it is packed in a kier and boiled with NaOH (2 to 5% on the weight of goods) for 2 to 10 hours, after which it is washed with water in the kier. Care must be taken that goods saturated with caustic do not touch hot iron. Residual alkali may be neutralized with a dilute acid, followed by thorough washing with water.

LAUNDRY AND HOME BLEACHING

The preceding discussion of the preparation and bleaching of cotton has been confined to the commercial production of a market bleach, that is, white cotton yarn or cloth that is to be made up into some form of white goods or to be dyed in light shades or used for making cotton prints. However, an enormous amount of bleaching is done in laundries and in the home, and we shall now consider the bleaching of cotton from these points of view.

One of the first things we discover is that calcium hypochlorite cannot be used. In the laundry or home, bleaching is done at a time when the wash has a great deal of soap in it, and if calcium hypochlorite were to be added, insoluble calcium soap would be precipitated on the goods. Therefore laundry bleaching is always done with sodium hypochlorite. One fact that many housewives (and some laundrymen) do not realize is that bleaching is not a cleaning operation; *bleaching will not remove dirt.* Bleaching is only a decolorizing or whitening reaction dependent on oxidation. When shirts with dirty cuffs are washed, it does no good whatever to add some extra bleach liquor. That will not remove the dirt from the cuffs. This rule does not apply to certain stains which can be decolorized by oxidation.

Many consumers have mistaken ideas about the chemicals that are used in laundries, and we hear vague references made to "strong acids," "corrosive alkalies," etc., which are entirely without foundation. The only chemical used in any laundry which can harm shirts, sheets, or tablecloths is the bleach, but it can do much harm unless it is intelligently used. Some laundries are very careful about alkali and builders, but careless with bleach. This can be attributed only to a lack of knowledge of bleach and the harm it can do. It is overbleaching in the laundry or at home that causes loss in strength of cotton goods, with the accompanying shortness of life. It is to be understood that, after bleach has oxidized coloring matter (and some stains), it will begin to attack cotton itself, forming oxycellulose and weakening the cotton.

Bleach for the power laundry can be purchased in the form of bleaching power (chloride of lime) or liquid bleach in carboys. Some laundries make their own electrolytic bleach. A convenient strength for a dilute bleach liquor for laundry use is 1%. This really means a solution containing 10 gm available chlorine per liter. Such a solution can be obtained by making a paste of 10 lb of bleaching powder, working it up with 20 gal water, and then stirring in 10 gal of water containing 20 lb of modified soda (a mixture of sodium carbonate and bicarbonate) or 10 lb of soda ash. Let the $CaCO_3$ settle and then draw off the supernatant liquid. Liquid carboy bleaches are simply diluted to 1%. The housewife must depend on bottled bleach liquor such as Clorox, Roman Cleanser, Linco, etc. These bleaches are labeled with the hypochlorite strength and should be used in proper amounts.

In power laundries the amount of bleach used is based on the dry weight of goods to be bleached, rather than on a solution of a certain strength. This is done because, after the consumption of bleach by coloring matter, the cotton is attacked. This is what we want to prevent. If a certain strength solution is used for a full load of goods and a similar solution for a small load, the cotton in the small load will be much more oxidized than that in the full load. The amount of bleach recommended is 2 qt of 1% bleach for each 100 lb of wash. A 1% bleach contains 10 gm available chlorine per liter, and as a quart is approximately equal to a liter, we may say that 20 gm chlorine should be used for each 100 lb of wash. These are much smaller amounts than would be used in the commercial bleaching where cotton is first bleached. Cotton that goes to the laundry has already been bleached, so that it requires less oxidation to keep it white.

It is probably not practical to weigh the home wash, and yet some approximation should be possible. Washing machines for home use are built to accommodate an average of about 8 lb (dry weight) of wash. This is about the equivalent of 4 sheets. The volume of water varies with types of machines, but usually runs from 12 to 15 gal. Let us assume that a load for home laundering is 8 lb and that the volume of water is 12 gal.

Suppose the housewife wants to use one of the popular brands of bleach sold in grocery stores. She buys a bottle, reads the directions carefully, and follows them accurately. How does her bleaching compare with that done in a commercial laundry? One brand containing 5.25% NaOCl recommends the use of 1 tablespoon of bleach for each gallon of water, which would be 12 tablespoons for one load of wash. This is equal to 6 oz or ¾ cup. Bleach containing 5.25% NaOCl is the same as 50 gm/l of available chlorine, or about 1.5 gm chlorine per ounce, and 6 oz would contain 9 gm available chlorine. If the bleaching were done in a power laundry, how large a wash could be done with this amount of bleach? We found that good laundry bleaching practice uses 20 gm chlorine for 100 lb dry wash. Therefore 9 gm chlorine would be enough to bleach a load of 45 lb. If the home bleach directions are followed, 9 gm chlorine will be used for only 8 lb. The only logical conclusion is that the laundry uses only about one-fifth as much bleach as the housewife, and, therefore, it is just as logical to assume that there will be only one-fifth as much chance for damage and loss of strength due to oxidation of cotton. It would seem that the housewife might use much less bleach.

One brand of grocery store bleach recommends that if the wash is extra dirty it may be soaked overnight in soap with bleach added (1 cup for 10 gal of water). This means 12 gm available chlorine, which is enough to bleach 60 lb of wash in 30 minutes. Overnight bleaching with such an amount of chlorine is not only foolish but dangerous. It must be remembered that bleach is not a cleanser. It is only a whitener. Extra dirty clothes cannot be cleaned by using more bleach or soaking for a long time. The only way to remove dirt is to wash the clothes with a real detergent. Bleaching should follow this washing.

Another thing to be considered is the manner of adding the bleach. The laundryman adds it as a 1% solution, the total amount of chlorine being only one-fifth as much as is added in the home laundry. It is bad practice to add the bleach directly to the load in the machine and then to start the machine, because bleach begins to react very quickly, and local overbleaching is almost certain to occur before the bleach can be distributed through the entire volume. The laundryman has special ways for taking care of this, but it would be much better in the home to lift the load, add bleach to the water or suds, stir well, and drop the load into the water.

Another factor involved in home bleaching is rinsing. In commercial laundries, the goods are rinsed several times after bleaching to remove unused bleach as completely as possible. It is common knowledge that rinsing in the home laundry is much less efficient. It must be remembered that the oxidizing effect of hypochlorite is a cumulative one that continues as time goes on. If some bleach is left in cotton goods because of poor rinsing, the bleach will continue to oxidize the cotton, and the chance for loss of strength will increase.

Power laundries treat the goods with a sour after bleaching, which serves three purposes. (1) All sours are weakly acidic compounds and therefore will neutralize any alkalinity that may have been retained by the wash. This is desirable because residual alkali might cause damage when the goods are ironed, and because the tendency for starch to turn yellow is accentuated by alkali. (2) Most sours will destroy excess or unused bleach, and for this reason are called anti-chlors. This is one of the most important functions of a sour. (3) Some sours act as stain removers.

Some typical sours and anti-chlors are acetic acid, which is perfectly safe; sodium bisulfite, $NaHSO_3$, which is a safe anti-chlor but may leave a bad odor; and sodium acid fluoride and sodium silicofluoride, which are also used, the former being an efficient iron rust remover. If these fluorides are not completely removed by rinsing, sharp irritating odors will be produced when the goods are ironed. Oxalic acid is a sour that is very widely used. The Laundryowners National Association recommends the following sours and procedure as being satisfactory and safe for laundry use:

> 1 lb oxalic acid in 1 gal hot water. Add 1 gal half glacial acetic acid and half water to the oxalic acid solution when cool. Use ½ pt of this mixture for 100 lb of wash. Rinse well.

Another bleaching agent coming into use is sodium chlorite, $NaClO_2$. White, Taylor, and Vincent[10] state that chlorine is not formed when solutions of sodium chlorite are acidified, but the product is ClO_2. They also claim that, when $NaClO_2$ is used as a bleach at a *p*H of 4, it is probably the chlorite ion that accomplishes the oxidation of coloring matter. The main advantage in the use of chlorite for bleaching cotton is that it will oxidize the coloring matter but will not attack the cellulose. There appears to be no chain-shortening action, because there is no loss in strength of the cotton, nor is there any decrease in cuprammonium viscosity. Jeanes and Isbell[11] found that chlorites can oxidize reducing sugars, but if the terminal oxygen is linked to two carbons, as it is in the anhydroglucose unit of cellulose, no oxidation takes place. When hypochlorites are used for bleaching there is danger of chain rupture, and care must be taken to protect the cellulose. However, when sodium chlorite is used, only the coloring matter is destroyed, and the cellulose is not affected. For general bleaching purposes, sodium chlorite should be used at a *p*H of 3 to 4, with an available chlorine content of 0.75 gm/l at about 70° C.

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[10] *Ind. Eng. Chem.*, **34**, 782 (1942).

TESTS FOR OXYCELLULOSE

The bleaching of cotton, either during the preparation of white goods for the market or in repeated launderings over a period of time, always results in the formation of some oxycellulose. In these oxycelluloses there appears to be no structural disintegration of cotton fibers, and yet there is always a small but significant rise in the copper number. It would therefore appear that the copper number could be used as a measure of the extent of oxidation; that is, by determining the copper number, one might tell whether the damage to cotton was caused by oxidative attack. However, we must remember two things, (1) the effect of boiling with alkali on the copper number, and (2) the effect of the *p*H of the oxidizing bath (page 144). When oxycellulose is boiled with alkali, the reducing property is decreased to practically the same as unoxidized cotton. Thus there is the possibility that serious oxidation may have taken place, but previous to the copper number determination the material may have been subjected to the action of hot alkali. In such a situation, conclusions drawn from the size of the copper number would be misleading. On the other hand, we know that oxycellulose has an increased affinity for basic dyes such as methylene blue, and it happens that the methylene blue absorption is changed very little by alkali boiling.

The use of these quantitative values as criteria for extent of oxidation is complicated by the fact that they are dependent on the

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[11] *J. Research Natl. Bur. Standards*, **27**, 125 (1941).

*p*H of the oxidizing bath (page 144). Two samples of cotton may have consumed the same amount of oxygen, and yet one may have a high copper number and a low methylene blue number, and the other sample have a small copper number. Furthermore, the methylene blue test is not so sensitive as the copper number test.

This sounds quite complicated, but we can still learn much about the past history of cotton goods by means of these two values, if they turn out to be what we might call positive values. Let us discuss some examples. Cotton cloth A has a low copper number and a low methylene blue number. This does not tell us much, as the cloth may have been oxidized considerably in an acid bath (low methylene blue number) and then heated with alkali before being analyzed. Cloth B has a high copper number. That settles the matter. In such circumstances the methylene blue number will not even be determined. Cloth C has a low copper number. The methylene blue number must then be determined. If it is high, there are two possibilities: (1) that the cloth has been treated with hot alkali (decreasing the copper number) or (2) that it has been oxidized in a bath of the alkaline type. The summary of these examples tells us that positive results can be interpreted logically, but negative results cannot. Copper number is the better test for acid-oxycelluloses (unless they have previously been treated with hot alkali), and the methylene blue number is the better test for alkaline oxycelluloses.

Both copper number and methylene blue number are criteria of chemical change in cotton, the copper number being associated with increased number of reducing groups, and the methylene blue with increased number of carboxyl groups. There are other tests which show increased reducing groups. Among these are (1) dyeing with Indanthrene Yellow (Ermen[12]); (2) staining with Nessler's solution (Ditz[13]); (3) staining with $AgNO_3$ (Harrison[14]); and (4) the effects of heat and hot 1% NaOH solution. These are definitely associated with high reducing power and, therefore, high copper number. Such oxycellulose will scorch at a lower temperature than unoxidized cotton, and will turn yellow when boiled with 1% NaOH solution. However, a cotton cloth may have suffered a considerable tendering and yet not give positive results with these tests. Such an oxycellulose would be one that had been oxidized in alkaline medium. It would have a high methylene blue number.

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[12] *J. Soc. Dyers Colourists*, **28**, 132 (1912).

[13] *J. prakt. Chem.*, **78**, 343 (1908).

[14] *J. Soc. Dyers Colourists*, **28**, 359 (1912).

All the preceding tests are based on the existence of oxidized surfaces in which cotton has been chemically modified and the properties of which are changed by alkali treatment. The measurement of the viscosity of cuprammonium solutions of cotton is a physical test free from the preceding limitations. It is a sensitive indication of oxidative attack, regardless of the presence or absence of a chemically changed surface, or the type of oxidation (acid or alkaline), or of subsequent treatment of the material. It has been shown that the decrease in viscosity is a function of the oxygen consumed, and that subsequent boiling with alkali does not restore the high viscosity. Viscosity is a sensitive test for the early stages of oxidation, as is the copper number. All technically bleached cotton has a lower viscosity and higher copper number than unoxidized cotton. However, a difference must be noted in what can be learned from the two tests. Suppose a cloth consumes 0.2% oxygen during bleaching. It will have a certain copper number and viscosity. Then suppose it is treated with hot alkali and bleached again so as to absorb 0.2% oxygen. It will now have about the same copper number as before, but its viscosity will be much lower. As a result of these two oxidations, the cotton will have suffered considerable loss of strength, which could be demonstrated by a viscosity determination, but not by copper number. Viscosity of cuprammonium solutions of cotton is the most useful test for injury caused by oxidative attack during bleaching. However, it is not discriminating, because it is a measure of average chain length, and chains may be shortened by acid hydrolysis as well as by oxidation.

Clibbens and Geake[15] recommend a rapid method for testing bleached goods. It consists of determining the specific viscosity of a 0.5% cuprammonium solution of the cotton with a mixture of glycerin and water having a specific gravity of 1.1681 (time of flow of cotton solution ÷ time of flow of glycerin). The time of flow of this particular glycerin solution is the same as that of a cuprammonium solution of a cotton that has suffered the maximum amount of damage due to bleaching. Therefore, if the specific viscosity of the cotton is greater than 1, the cloth has been overbleached, but if the specific viscosity is less than 1 it is all right, and the smaller this value, the better.

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[15] *J. Textile Inst.*, **19**, T77 (1928).

Clibbens and Geake also express results in terms of fluidity (see page 129) and find that a fluidity of 10 corresponds to about 10% loss in tensile strength, and a fluidity of 20 to about a 20% loss in strength. The fluidity of normally bleached cotton varies between 2 and 7. Values higher than 7 indicate bad overbleaching.

A study of these tests for oxycellulose makes it apparent that they are quite similar to the tests for hydrocellulose (page 135). We are therefore faced with the problem of distinguishing between hydrocellulose and oxycellulose. That is, how can we demonstrate the difference between cotton that has been modified by acid hydrolysis and cotton that has been damaged by oxidation? It appears that the best methods must be based on the fact that very few carboxyl groups are formed during acid hydrolysis of cotton. We have already found (page 142) that the carboxyl groups of oxycellulose can be converted into CO_2 by decarboxylation. Krajcinovic[16] describes a reaction that can be used to distinguish between oxycellulose and hydrocellulose. It is based on the fact that COOH groups will react with aromatic diamines, and the product can then be diazotized and coupled. For example, cotton may be moistened with an alcoholic solution of benzidine, let stand a few minutes, and then rinsed well. It is then diazotized by treating with hydrochloric acid and sodium nitrite. After the sample has stood for a few minutes, it is rinsed and spotted with a few drops of an alkaline solution of β-naphthol. Oxycellulose will give a bright red color, whereas hydrocellulose will not. Negative results obtained by this test are not conclusive, because oxycelluloses of the reducing type have only a few carboxyl groups. However, positive results are definitely indicative of oxycellulose.

The Action of Cotton with Alkalies. Mercerization

In Chapter 6 (page 161) we discussed the chemical aspects of the action of alkalies on cellulose, and in this chapter we shall study the physical changes that occur when cotton is mercerized. In April 1851, John Mercer was granted British Patent 13,296, in which he claimed to have been the inventor of the processes of "the subjection of cotton, linen and other vegetable fibrous materials, either in fibre form or any other stage of its manufacture, either alone or mixed with silk, woolen or other animal fibrous material, to the action of caustic soda or caustic potash, dilute sulfuric acid, or solution of chloride of zinc of a temperature and strength sufficient to produce the new effects, and give to them the new properties above described, either by padding, printing or steeping, immersion or any other mode of application."

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[16] *J. Textile Inst.*, **38**, T11 (1947).

This was the beginning of one of the most important advances that have ever taken place in the textile field, the birth of mercerized cotton. An enormous amount of research has been done since that time on the action of alkalies on cotton, but not much has been added to the original list of observations made and patented by John Mercer. The main points in his alkali treatment of cotton are:

1. Shrinkage in the length of yarn or the area of cloth.
2. Increase in tensile strength.
3. Increase in absorption of dyestuffs.
4. Increase in physical compactness of yarn and cloth.
5. Increased water absorption.
6. Increased reaction at lower temperatures.
7. Preferential absorption of NaOH during the process.
8. Possible compound formation.

Mercer's alkali-treated cotton had all these properties, and yet it was never a commercial success. Apparently the cotton trade was not interested in these new effects, and forty years passed before any modification of Mercer's process was made which enjoyed commercial success. In 1890 Horace Lowe was granted British Patent 4452, in which he claimed the production of luster on cotton cloth or yarn by holding it under tension during the process of alkali treatment, with subsequent washing, or stretching it after alkali treatment. This luster-producing process for treating cotton was so successful that today the mercerization of cotton is a huge business.

Luster is purely a surface property, the reflection of light from a smooth surface; the smoother the surface, the greater the luster. Therefore when cotton is mercerized under tension, its surface must be rendered smoother. Not only does surface smoothness enter into luster but, when fine filaments are to be twisted together, the cross-section area is an important factor. So let us compare individual cotton fibers according to physical appearance, surface, and cross-section. Table 28 shows this comparision.

TABLE 28

Cotton under the Microscope

	Unmercerized	Mercerized without Tension	Mercerized with Tension
General appearance	Flat ribbon with spiral twists	Much rounder, with no twist	Like a smooth cylindrical rod
Surface	Rough, not uniform	Much smoother, more uniform, but high magnification shows creases and wrinkles	Smooth and free from folds and creases
Cross-section	Irregular ear-shaped	Oval	Good circle
Lumen	Broad, irregular	Contracted	Contracted to a mere point

It is interesting to know what physical change takes place during the treatment of cotton fibers with NaOH of different concentration. Pope and Hubner[17] give the following:

Up to 6.5% NaOH	No change
7.0–8.0	A little untwisting in 1 second
8.8	Rapid untwisting at first, then slowly
11.6	Rapid untwisting during first 5 seconds
15.8	Complete untwisting, followed by swelling
17.8	Untwisting and swelling together
26.7–36.4	Swelling first and then untwisting

It is found that 17.5% NaOH is the lowest concentration that will show a substantial increase in luster. If the preceding behavior of cotton is considered along with this, we might conclude that the production of luster is dependent upon swelling and untwisting occurring simultaneously or upon swelling preceding untwisting, but that the swelling of an untwisted fiber will not produce luster.

The amount of shrinkage in yarn when it is subjected to the action of NaOH of various strengths is considered to be important. It is not very reliable as a measure of mercerizing effect because other factors, such as structure of the yarn, changes in fiber diameter, slippage of fibers, etc., enter in. Nevertheless, the concentration at which maximum shrinkage takes place is of great importance. Therefore we can use shrinkage as a good measure of mercerizing efficiency, and study the five factors that control mercerization. These factors are concentration of NaOH, time, temperature, tension, and type of cotton goods. Table 29 shows the relations of the first three factors. All figures are in per cent shrinkage. The figures show clearly that mercerizing effects decrease with rise in temperature, and that ordinary room temperature is the most practical. The figures also show that nothing is gained by prolonging the treatment beyond 10 minutes. The one-minute shrinkage is entitled to some comment. It shows that shrinkage in alkali takes place very rapidly. This is important to remember, because, in any processing of cotton where alkali is used, any local increase in strength of alkali may cause considerable shrinkage at that point. So far as concentration of NaOH is concerned, the figures show that 21 to 23% NaOH is the best. There is no practical advantage to be gained by using a 29% solution.

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[17] *J. Soc. Chem. Ind.*, **23**, 404 (1904).

TABLE 29

SHRINKAGE OF COTTON IN NaOH*

°C	Concentration of NaOH											
	10%			19%			24%			29%		
	Time, minutes											
	1 minute	10 minutes	30 minutes	1 minute	10 minutes	30 minutes	1 minute	10 minutes	30 minutes	1 minute	10 minutes	30 minutes
2	12.2	15.2	16.8	19.2	20.1	21.5	22.7	22.7	23.5	23.5	23.0	23.0
18	8.0	8.8	11.8	19.2	20.1	21.1	22.5	22.5	22.5	23.5	23.0	21.0
30	4.6	4.6	6.0	19.2	20.3	19.0	19.8	19.8	19.8	20.7	20.5	20.1
80	3.5	3.7	3.8	13.7	14.2	15.5	15.5	15.5	15.5	15.5	15.5	15.4

* Marsh, *Mercerizing*, D. Van Nostrand Company, 1942, p. 99.

The tension factor in mercerizing can be summarized as follows: mercerizing without tension causes a good increase in strength (25 to 30%) but no increase in luster. Mercerizing with tension great enough to prevent shrinkage produces the same increase in strength, and the luster is increased very much.

The type of cotton material to be mercerized is so varied that it is impossible to make any quantitative statements about it. Nevertheless, a few generalizations are of interest. Perhaps the most important facts to remember are that the object of mercerization is the production of luster; that this is obtained by the use of tension; that the larger the proportion of fibers lying lengthwise of the yarn, the better the luster will be.

The cotton fiber itself is the fundamental unit in yarn or cloth, and so it should be considered first. The long, fine-staple cottons are best for mercerizing because they can be combed and spun into yarns with small amount of twist, and the individual fibers lie fairly parallel lengthwise of the yarn. Therefore, Egyptian, sea island, and Pima cottons are quite suitable for mercerizing.

After a yarn is spun, numerous loose ends of fibers protrude from its sides. If the yarn is gassed (run rapidly through a flame), these will be burned off and will leave a smooth surface. It would be impossible to subject these loose ends to tension during alkali treatment.

Spinning twist is another factor. In a tightly twisted yarn, the length of individual fibers is disposed more crosswise of the yarn than lengthwise, and therefore will not mercerize as well. The more loosely a yarn is twisted, the better it is. The best results will be obtained with yarns that have the lowest amount of twist and still retain enough adhesion to give them practical strength. This emphasizes the desirability of long staple cotton, because the extra length makes possible the spinning of such a yarn.

Two-ply yarns are better than singles, but only if the doubling twist is opposite to the twist in the singles. That is, if a yarn is spun with a right-hand twist, and two of these are folded with a left-hand twist, the folding will untwist some of the singles. The result is that a larger proportion of the fibers lie lengthwise of the yarn.

If cloth is to be mercerized, a faced cloth such as sateen will show the greatest increase in luster. This is because the long floats will lend themselves to the effect of tension more readily than shorter crossings of yarns.

Various attempts have been made to modify and improve the Mercer-Lowe process for mercerizing cotton. One such is described in U.S. Patent 2,390,032 (1945), assigned to Rohm and Haas, by which cotton cloth is treated with acrylonitrile first, and then with NaOH (10–20% solutions) for one hour. The cloth is then subjected to tension while it is washed and dried. It is claimed that the tensile strength of cloth so treated is increased 57%, whereas without the acrylonitrile the increase is only about 28%.

PROPERTIES OF MERCERIZED COTTON

Mercerization of cotton yields a product that, so far as modification is concerned, is about the same as unmercerized cotton. That is, the average chain length, reducing property, carboxyl content, etc., are the same. This is shown by the accompanying figures for Egyptian cotton (Sakellarides). However, the activity of cotton in all treatments is increased by mercerization. Mercerized cotton can be hydrolyzed and oxidized more easily, and is more soluble in Schweitzer's reagent. Its absorptive properties have been increased so that it will absorb more direct dyes and more water and iodine (the latter can be used as a qualitative test).

Properties of Egyptian Cotton

	Unmercerized	Mercerized
Copper number	0.01	0.01
Methylene blue number	1.17	0.96
Loss in weight in alkali	1.32	1.23
Fluidity	3.68	3.70

TABLE 30

Moisture Content of Mercerized Cotton

(Percentage moisture on dry weight of yarn)

NaOH used, %	Gray Yarn	Bleached Yarn
0	6.62%	5.51%
2.0	7.11	5.92
4.2	6.99	6.13
8.8	7.56	6.71
13.0	9.50	9.64
17.8	10.25	10.70
22.3	10.85	11.42
26.8	11.45	11.20

Schwalbe[18] proposed a hydrolysis number to express the increased ease of hydrolysis of mercerized cotton. Birtwell, Clibbens, and Geake[19] proposed a reactivity ratio to express the increased susceptibility to oxidation.

Mercerized cotton is more hygroscopic than unmercerized cotton; that is, it will absorb more water, and its normal moisture content is higher. This property is related to the strength of

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[18] *Z. angew. Chem.*, **21**, 1321 (1908).

[19] *J. Textile Inst.*, **21**, T85 (1930).

NaOH used in the treatment. Many investigations of this behavior have been made. Table 30 gives results obtained by Hubner and Wooton.[20]

Mercerized cotton has an increased affinity for direct dyes, which is governed by the strength of NaOH used in the process. Knecht[21] made quantitative determinations of the absorption of Benzopurpurin 4B from boiling solutions of the dye. He found that there is a steady increase in dye absorption, with increasing NaOH concentration until 25% is reached, after which the increase is much less. Some of these figures are given in Table 31. Knecht suggests that absorptions of Benzopurpurin 4B may be used as a qualitative test for mercerized cotton in which depths of color may be compared. The test can be made more sensitive if the dyed samples are carefully treated with dilute acid. The red color on unmercerized cotton will turn blue, but mercerized yarns will retain their red color. Excess acid must be avoided.

TABLE 31

Absorption of Benzopurpurin 4B by Alkali-Treated Cotton

NaOH in Solution, %	Dye Absorption, gm, per 100 gm Cotton
0	1.77
8.5	2.39
11.0	2.57
15.5	3.02
17.5	3.15
20.0	3.27
22.5	3.38
25.0	3.50
29.0	3.60
31.5	3.66

Increased absorption of iodine by mercerized cotton was studied by Hubner.[22] He measured the actual amounts absorbed by mercerized and unmercerized cotton, but his most important observation was that the absorbed iodine could be rinsed out of unmercerized cotton much faster than from mercerized cotton, and he suggested this as a test for mercerized cotton. Hubner also found that the sensitivity of the iodine test could be improved by using iodine solutions with zinc chloride.

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[20] *J. Soc. Chem. Indust.*, **41**, 10 (1925).

[21] *J. Soc. Dyers Colourists*, **24**, 67 (1908).

[22] *J. Soc. Chem. Ind.*, **27**, 105 (1908).

NEW FINISHES ON COTTONS

Since 1933 the cotton textile industry has been revolutionized by the development and use of new finishes. We are all acquainted with lacquer or surface coating finishes which have been in use for many years, but these new finishes are not of that type. They are applied from water solutions or dispersions and penetrate to the interior of yarns, or perhaps even into the cotton fibers. Thus all the desirable properties of a cloth are retained. Its porosity, absorbency, feel, and flexibility are usually not affected, and it has all the characteristics of the untreated cloth. However, it may have new and improved properties such as strength, luster, and resistance to water, crushing, and abrasion. On the other hand, entirely new effects can be obtained. The available finishing materials include a wide variety of compounds, which may be applied by a number of methods. Thus, by the proper selection of finishing substances, used in certain concentrations and applied by the proper methods, a wide variety of effects can be obtained. In fact, the same compound can be used to produce different effects by merely changing such factors as concentration, temperature, solvent, etc.

The new finishing substances are being used today to produce millions of yards of cotton and rayon cloths which have increased tensile strength and wearing qualities. The luster, elasticity, and elongation of yarns can be increased or decreased, whichever is more desirable. Cotton cloths can be given the luster of silk, the absorbency and coolness of linen, or the stability of high-grade worsteds. Spun rayons may be given the quality, character, and resiliency of good woolens.

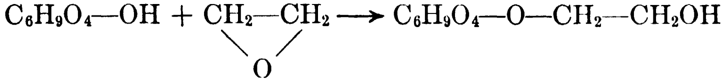
A large number of these finishing materials have been put on the market and are being used in huge amounts. For most processes only small amounts of them are necessary, and yet their total commercial consumption is much greater than the old coating or lacquer types of finishes which went into such things as oilcloth, tarpaulins, artificial leather, table covers, etc. We shall divide these finishing compounds into three main groups: the cellulose ethers, quaternary ammonium compounds, and formaldehyde resins.

The cellulose ethers were discovered by Lillienfeld, a Polish chemist, who patented their use for finishing cottons. These compounds can be made from cellulose by the use of four different reagents, all of the reactions taking place in the presence of NaOH.

Alkyl chlorides can be made to react with cellulose,

$$C_6H_9O_4{-}OH + RCl \longrightarrow C_6H_9O_4{-}O{-}R + HCl$$

A hydroxy ethyl ether of cellulose can be made in two ways, (*a*) by the use of ethylene oxide,



$$C_6H_9O_4{-}OH + \underbrace{CH_2{-}CH_2}_{O} \longrightarrow C_6H_9O_4{-}O{-}CH_2{-}CH_2OH$$

and (*b*) by treating cellulose with chlorohydrin.

$$C_6H_9O_4{-}OH + Cl{-}CH_2{-}CH_2OH \longrightarrow C_6H_9O_4{-}O{-}CH_2{-}CH_2OH + HCl$$

And, finally, a carboxylic ether can be made by the action of sodium chloroacetate on cellulose.

$$C_6H_9O_4{-}OH + Cl{-}CH_2{-}COONa \longrightarrow C_6H_9O_4{-}O{-}CH_2{-}COONa + HCl$$

The amount of substitution in cellulose can be regulated by the proper control of the reactions, so that ethers of different solubilities can be made. For example, if one OH group of every two glucose units is etherified, the product will be insoluble in water but soluble in NaOH. If one OH group of each glucose unit is etherified, the substance will be water-soluble, and upon higher etherification the ethers will be soluble in many organic solvents.

The cellulose ethers are white fluffy substances similar to cotton linters. When they are applied to cotton they are usually dissolved in 6 to 10% NaOH solutions so as to make about a 6% solution of the ether. Cotton cloth is passed through the solution at temperatures below 15° C until the proper amount of impregnation has taken place, and then the ether is coagulated by passing the cloth through an acid bath. A variety of permanent finishes can be obtained in this way, from soft and silky to stiff, firm, and crisp. This stiffness is durable and permanent, as contrasted with the temporary effects obtained with starch. One of the main advantages to be gained by finishing with cellulose ethers is the resistance to repeated launderings. Goldthwaite, Smith, and Barnes[23] have treated cotton goods with a solution of cellulose ether in cuprammonium instead of NaOH. They use cellulose hydroxy ethyl ether, immerse the goods in a cold solution, squeeze out, and dry without rinsing at 180° F. Cloth treated in this way has the usual properties and in addition is found to be rot- and mildew-proof. British Patent 477,029 describes a water-repellent finish that is obtained by treating cloth with high molecular weight aldehydes, such as stearyl aldehyde ($C_{17}H_{35}CHO$). The cloth is immersed in a 0.5% solution of the aldehyde in a low-boiling hydrocarbon, dried, and heated for 5 minutes at 150° C. The cellulose ethers in general have been successfully applied to damask cloths to produce a smooth lustrous finish and a large reduction in linting during use. These finishes require no starch after laundering.

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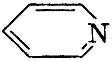
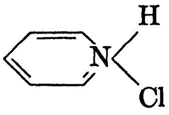
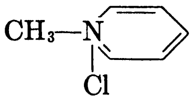
[23] U.S. Patent 2,417,869 (1947).

There is some confusion among the terms used in discussing fabrics that have been treated to protect them and the wearer from water. A *waterproofed fabric* is one which is impervious to both water and air, which means that all interstitial openings in the cloth have been closed by some treatment or other. Garments made from such fabrics are very uncomfortable because they lack ventilation. On the other hand, *water-repellent fabrics* are resistant to water but pervious to air. The yardage of cloth treated to give water-repellency is enormously greater than the yardage of waterproofed fabrics, so that we shall confine our discussion to the water-repellent treatments.

Some of the best water-repellent finishes are produced on cotton and rayon fabrics by the use of nitrogen compounds which are cation-active agents. A cation-active compound is one which may be very complex, but somewhere in the molecule there is a polar arrangement (like a salt), the cation (positive) part of which is associated with the main part of the molecule. For example, one of the important classes of such compounds is the quaternary ammonium salts of pyridine, C_5H_5N, or . It will be seen that pyridine is a tertiary amine (page 49) and therefore will form salts with acids, e.g., pyridinium chloride.

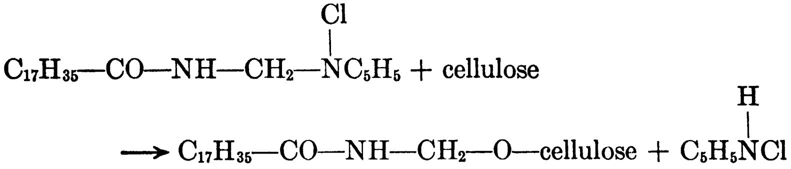


A quaternary ammonium salt is one in which a nitrogen atom is attached to organic groups by four valence bonds, such as R_4NCl or



These compounds behave like ordinary inorganic salts.

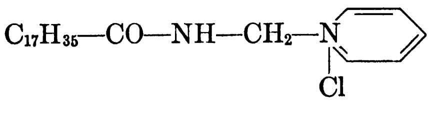
Zerner and Pollak[24] studied the chemical reaction that takes place when cellulose is treated with a quaternary salt, such as a pyridinium salt, and then baked or cured at a high temperature. All of these quaternary salts suitable for water-repellent treatments must have two distinctly different parts in the molecule. The real water-repellent (or hydrophobic) part of the molecule is a long-chain fatty acid derivative containing 15 or more carbons. This chain may be saturated or unsaturated. The other part of the molecule is the polar cation-active part which can react with the OH group of cellulose. The reaction given below shows what happens during the curing (heating) of a cotton cloth that has been treated with stearamido methyl pyridinium chloride,



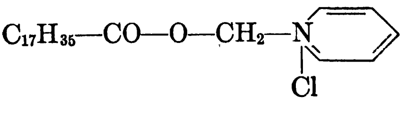
$$C_{17}H_{35}\text{—CO—NH—CH}_2\text{—}\overset{\text{Cl}}{\overset{|}{\text{N}}}C_5H_5 + \text{cellulose}$$

$$\longrightarrow C_{17}H_{35}\text{—CO—NH—CH}_2\text{—O—cellulose} + C_5H_5\overset{\text{H}}{\overset{|}{\text{N}}}\text{Cl}$$

The practical pyridinium salts used in the United States are either substituted amides or esters of stearic acid, $C_{17}H_{35}COOH$. For example,



stearamido methyl pyridinium chloride, or



stearoyl oxymethyl pyridinium chloride.

Compounds of this general type are applied to cotton goods from water solutions or dispersions, after which the cloth is dried on a tenter. The material is then baked or cured in order to complete the chemical reaction and leave the fabric impregnated with an insoluble water-repellent substance. Finishes so obtained are usually durable to laundering and dry cleaning.

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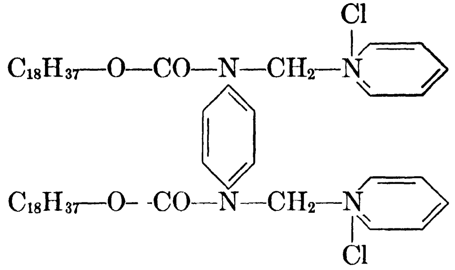
[24] *Textile Research J.*, **14**, 242 (1944).

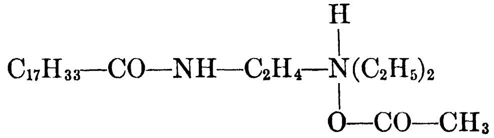
The Imperial Chemical Industries of England[25] proposes the use of a new type of quaternary ammonium salt which is a sort of double pyridinium salt made from esters of chloroformic acid, such as Cl—$COOC_{18}H_{37}$, octadecyl chloroformate. Such an ester is treated with *p*-phenylenediamine, then with formaldehyde and HCl, and finally with pyridine. The final product would have the structure,



Another group of quaternary salts that has been found satisfactory for producing water-repellent finishes is known as the sapamines. They are derivatives of oleic acid (an unsaturated acid, $C_{17}H_{33}COOH$). They are substituted amides of oleic acid, but differ from the first group discussed in that they are substituted ethyl amides instead of methyl amides, and organic groups attached to nitrogen are aliphatic rather than aromatic.

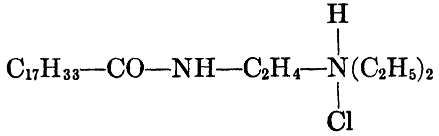
The sapamines are manufactured in the form of acetates, chlorides, and sulfates. Examples are

Sapamine A
(an acetate)



$$C_{17}H_{33}-CO-NH-C_2H_4-\overset{H}{\underset{O-CO-CH_3}{N}}(C_2H_5)_2$$

Sapamine CH
(a chloride)



$$C_{17}H_{33}-CO-NH-C_2H_4-\overset{H}{\underset{Cl}{N}}(C_2H_5)_2$$

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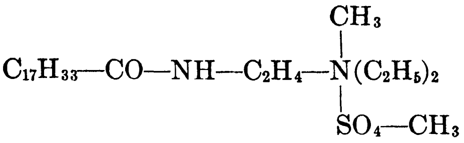
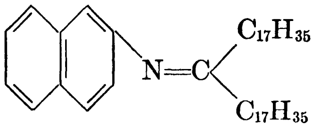
[25] U.S. Patent 2,386,141 (1945).

Sapamine MS
(a sulfate)



$$C_{17}H_{33}\text{—CO—NH—}C_2H_4\text{—}\overset{\displaystyle CH_3}{\underset{\displaystyle SO_4\text{—}CH_3}{N}}(C_2H_5)_2$$

Another class of nitrogen compounds suitable for making cotton goods water-repellent is disclosed by Zerner, Davies, and Pollak.[26] This is a group of Schiff's bases. A Schiff's base is obtained by the well-known reaction between aldehydes or ketones with primary amines. Ketones when used for this purpose must have 8 to 20 carbons on each side of the carbonyl group, and the amine must have at least 8 carbons or be an aromatic primary amine. An example of a Schiff's base made from β-naphthylamine and diheptadecyl ketone is



These compounds are applied from solutions in an organic solvent in the cold, dried, and heated for 5 minutes at 120–160° C.

Since about 1940 the use of synthetic resins for finishing cotton goods has been developed to a point where millions of yards of cloth are going onto the market with resin-impregnated finishes. The characteristics of cloth can be changed without changing its appearance. The use of as much as 25% resin will leave the cloth with the same appearance and feel as it would have without the resin. However, the properties which determine its durability and serviceability will be improved by the resin. One novel feature of resin finishing is that the same resin may be used to obtain different effects, depending on the method of application. If it is dissolved in a solvent and applied to the surface of cloth, the result is a coating which may be varied by the use of different concentrations of resin. If it is applied as a dispersion in water it will impart a lustrous finish, and if applied from water solutions, it makes fabrics more resilient.

In addition to the preceding modifying effects, other, and perhaps more desirable, results can be attained by resin treatments. It is possible to make fabrics water-repellent so that they require less frequent and easier laundering. Some of the most important creaseproofing methods are based on the use of such resins. When applied to wool fabrics the shrinkability, as well as its felting property, is very much decreased. Such finishes will eliminate much of the wrinkling of spun rayon dress goods and reduce the tendency of knit goods to bag and get out of shape. No one resin can accomplish all these results, but it is very seldom that all of them would be required in the same fabric. The manufacturer has a wide variety of resins from which to select the one best suited for the particular cloth he is producing.

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[26] U.S. Patent 2,413,024 (1946).

Four main classes of resins can be used in finishing textile fabrics. They are all sold in the form of formaldehyde condensation products, which are either monomers or polymers of low molecular weight. In every instance, after these condensation products are deposited on the fabric, they are polymerized or resinified by heat. The four types of condensation products are made from formaldehyde with phenol, urea, melamine, or acetone. The first of these is rather undesirable because of its inherent tendency to discolor.

If we are to study the use of resins in finishing textile materials, we should consider all the possibilities, even though they may not have achieved much commercial importance. A very good review of this subject[27] divides them into two main classes, based on their solubility and the effect of heat on them. These two divisions are the thermosetting and thermoplastic resins. Thermosetting resins are those that harden when sufficient heat is applied and thereafter are practically infusible and insoluble. Thermoplastic resins are those that are softened by heat and dissolved by certain organic solvents.

The four types of resins previously mentioned are subdivisions of the thermosetting class. In addition to these are the alkyd or glyptal resins. They are the products of the condensation of dibasic acids with dihydric alcohols (page 34).

The thermoplastic resins can be subdivided into the polyvinyl resins, the acrylates (and methacrylates), and the polythenes and polyamides. The polyvinyls include the chlorides, acetates, butyrates, and alcohols, or mixtures of them. They vary from hard, firm resins to soft, pliable ones, and therefore a wide range of finishes will run from crisp, stiff, papery finishes to soft, drapable, full-hand effects. The polythenes are produced by the polymerization of ethylene at high pressures. Tape made of polythene can be used for binding fabrics without sewing. The tape can be laid on between two cloths and heated. This fuses the tape and holds the two cloths together. The acrylates are applied from dispersions in water to give full, soft finishes. The methacrylates, dissolved in trichloroethylene, are used by dry cleaners as stiffening agents to overcome the limpness shown by some fabrics after dry cleaning.

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[27] *J. Soc. Dyers Colourists,* **61,** 269 (1945).

The formation of the urea-formaldehyde resins is based on the reaction between formaldehyde, $H_2C{=}O$, and amino groups, NH_2, as shown by the following equation.

$$R{-}NH_2 + H_2C{=}O = R{-}NH{-}CH_2OH$$

Urea, $H_2N{-}CO{-}NH_2$, has two NH_2 groups, which may react with formaldehyde one at a time. For example, one molecule of each will react to form $H_2N{-}CO{-}NH{-}CH_2OH$, known as monomethylol urea. As this compound still contains an NH_2 group, it will react with another molecule of formaldehyde to form $HO{-}CH_2{-}NH{-}CO{-}NH{-}CH_2OH$, dimethylol urea. Further heating of the reaction mixture forms high molecular weight thermosetting resins. Thus the unpolymerized condensation products can be applied to textiles from water solution, followed by a baking operation, which will form the insoluble resin. This polymerization can be controlled so that polymers of low, medium, or high molecular weight can be produced, thus permitting finishes of different properties to be obtained.

The word melamines is used in the plural to indicate that melamine itself or derivatives of it are used for finishing textile materials.

Johnstone[28] shows how melamine and its formaldehyde derivatives are made by the American Cyanamide Company. There are essentially four steps in the process: (1) Calcium carbide and nitrogen are heated to 220° C to form calcium cyanamide

$$CaC_2 + N_2 = CaNCN + C$$

(2) The free cyanamide is liberated by treating this calcium salt with a weak acid such as carbonic acid

$$CaNCN + HOH + CO_2 = H_2NCN + CaCO_3$$

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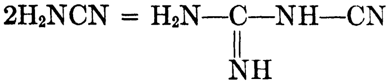
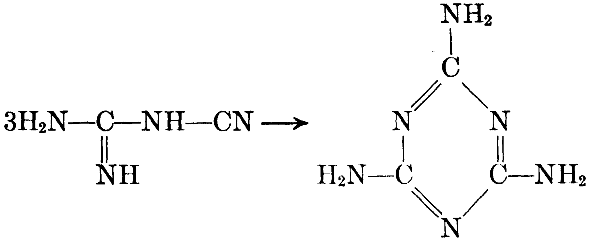
[28] *Am. Dyestuff Reptr.*, **33**, 301 (1944).

(3) Cyanamide is polymerized to dicyanamide

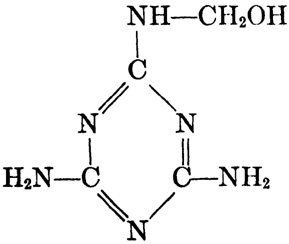


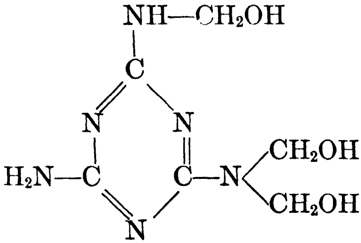
$$2H_2NCN = H_2N-\underset{\underset{NH}{\|}}{C}-NH-CN$$

(4) By the proper control of temperature and pressure, dicyanamide is converted into melamine



Derivatives of melamine can be prepared by condensing it with formaldehyde to form various methylolmelamines, just as urea does. An excellent discussion of the methylolmelamines[29] points out that melamine can resonate in many ways, so that the formaldehyde condensation products are even more obscure as far as their structures are concerned. However, theoretically speaking, each of the hydrogens of melamine may be substituted by a CH_2OH group, so that we have the possibility of mono-, di-, tri-, etc., up to hexamethylolmelamines. Two such formulas are shown here.





When melamine resins are baked (cured), it appears that two types of linkages are formed, the methylene linkage (through a CH_2 group) and the ether linkage (through an oxygen). It is claimed that the melamine resins have properties that cannot be attained by the urea-formaldehyde resins due to the triazine ring, that is, the six-membered ring with alternate carbons and nitrogens shown in the structural formula for melamine. Methylolmelamines are much less soluble in water than the methylolureas, and therefore their use is more limited where a water-soluble resin is required.

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[29] Society of Dyers and Colourists, *Fibrous Proteins Symposium*, 215–220, May 1946.

The first use of these synthetic resins for fiber modification in the United States was in 1933, at which time the firm of Tootal-Broadhurst Lee (Manchester, England) introduced an anti-crease process. This firm was the outstanding pioneer in this field. They showed that cotton could be impregnated with urea-formaldehyde resins of low molecular weight, the resin pressed in and then polymerized by a short baking at high temperature. This treatment resulted in such improved resilience that the goods did not crease easily.

We have mentioned the great variety of effects that can be obtained by the use of resins in the finishing of cotton. This is possible because of several variables. In order to understand this, let us look at the method of application and treatment, having in mind the factors which may be varied.

When cotton or rayon cloth is impregnated with resin, (*a*) the resin may be of such a low degree of polymerization that it is completely soluble in water; (*b*) it may have an intermediate degree of polymerization, but may still be soluble; (*c*) with increased amount of polymerization, it may be in a colloidal solution; and (*d*) with still higher polymers it may be in colloidal dispersion. All these types of resins can be still further polymerized by heat. Thus we see that the degree of polymerization of the resin and its manner of distribution in the impregnating liquid can be varied, and each variation will give its special effect on cloth. Another variable is the concentration of resin in the liquid; for some finishes 1% is used, and for others, 20 or 25%. The method of application can be varied. That is, a cloth may be impregnated with an 8% dispersion of resin and then run through squeeze rollers with only a light pressure; another cloth may be impregnated with a 16% dispersion of resin, followed by a tight squeeze which would press out some resin. It is possible for these two cloths to come out with equal amounts of resin, but in the end they will differ with respect to crush resistance, abrasion resistance, elongation, tensile strength, etc. In one method the excess resin left on the surface of the cloth may be removed before baking;

in another method it may not be removed, giving a much stiffer finish.

Statements have been made that resin finishes will reduce shrinkage without loss of tensile strength. Powers[30] tested several types of fabrics to show the difference between urea-formaldehyde resins and the melamines. He reports in general that both resins will reduce shrinkage in cotton, rayon, and wool cloths from 50 to 85%, but the melamines are somewhat more effective. It was found that the methylolmelamines increased the strength of spun rayon and wool considerably, but the strength of cotton was not changed. When urea-formaldehyde resins were used, the strength of spun rayon increased a little, but cotton lost about 15% of its strength. Some of his results are shown in Tables 32 and 33.

TABLE 32

EFFECT OF RESINS ON COTTON SHEETING*

Resin	Shrinkage, %	Tensile Strength
None	5.2	41.5
Urea-formaldehyde	2.8	37.5
Phenol-formaldehyde	3.0	41.3
Methylolmelamine	1.8	40.8

* Powers, *Ind. Eng. Chem., Ind. Ed.*, **37**, 188 (1945).

Sheeting impregnated, dried rapidly, and cured at 300° F for 15 minutes. Shrinkage determined after 1 hour washing at 180° F.

Let us summarize the production of resin finishes on cotton and rayon goods. The resin is dissolved or dispersed in water, and the cloth is impregnated with this liquid and then passed between squeeze rollers, after which it is baked at high temperature. This final heat treatment polymerizes the resin to a high degree, rendering it insoluble and permanently fixed within the cloth.

Since 1940 the use of spun rayon in ladies' dress goods has increased enormously; one reason for this is the development of resin finishes for such materials.

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[30] *Ind. Eng. Chem., Ind. Ed.*, **37**, 188 (1945).

TABLE 33

Effect of Resin Concentration on Tensile Strength*

Cotton Sheeting			Spun Rayon			Wool Flannel	
Resin, %	Tensile Strength, lb		Resin, %	Tensile Strength, lb		Resin, %	Tensile Strength, lb
	Urea-formaldehyde	Methylol-melamine		Urea-formaldehyde	Methylol-melamine		Methylol-melamine
0	90	90	0	85	85	0	46.5
1	88	96	1	89	89	5	63.4
3	88	95	3	96	93	10	62.7
7	70	90	5	89	97	18	59.0
10	67	88	10	88	105	24	45.1
15	65	88	15	85	106		

* Powers, *loc. cit.*

QUESTIONS

1. What is the difference between lint fibers and linters? What is each used for?

2. How do cotton fibers during growth differ in shape and structure from mature cotton fibers used for spinning yarns?

3. What is accomplished by ginning cotton? What are the products?

4. What are the botanical names for the important cottons? How do they differ from each other? On the average, which is the strongest, the longest, the finest?

5. What physical feature of cotton is mainly responsible for its spinning quality?

6. What is the moisture content of cotton under normal conditions of temperature and humidity?

7. How does its strength change with increase in moisture content?

8. What are the impurities in raw cotton?

9. What would you expect to be the results of the action of the following acids and conditions on cotton?

(*a*) Cold dilute HCl, for 5 minutes, and dried without washing.
(*b*) Dilute H_2SO_4, boiled 5 minutes, but dried after rinsing.
(*c*) Dilute H_2SO_4, boiled 5 minutes, and dried without rinsing.
(*d*) A spot of dilute H_2SO_4 on a cotton cloth, and dried without rinsing.
(*e*) Boiling acetic acid, dried without rinsing.
(*f*) Cold concentrated H_2SO_4 for 5 minutes and washed before drying.

10. What is the difference between viscosity values and fluidity values?

11. If a cotton cloth has been damaged by the action of acids, what will happen if a sample of the material is boiled with dilute NaOH?

12. How can paper be parchmentized?

13. What is the usual bleaching agent used for bleaching cotton? To what is the actual bleaching attributed? What type of chemical compound is the bleaching agent?

14. Why is chlorine water such a weak bleaching agent?

15. Give two ways in which sodium hypochlorite can be made.

16. How can the rate of bleaching cotton with hypochlorites be controlled?

17. Would bleaching action be hindered or made more efficient by immersing cotton in bleach liquor and then exposing it to the air? Explain your answer.

18. What connection is there between bleaching and detergent action? Discuss it.

19. In what forms are bleaching agents available to the power laundry? to the home laundry?

20. If bleaching is allowed to continue too long, what happens to cotton? What is the chemistry involved in this? What is the best way to add bleach in the home laundry?

21. About how much bleach (in terms of grams of available chlorine) is used for bleaching 100 lb of wash in a power laundry? In order to duplicate this proportion, what volume of a grocery store bleach liquor, containing about 5% NaOCl, should be used for an 8-lb wash in the home laundry?

22. Discuss causes for damage to cotton during preparation for bleaching by the lime boil method.

23. What is the purpose of sour and anti-chlor in bleaching?

24. How is cotton mercerized? Discuss the procedure. How does this change cotton? What is the optimum temperature and concentration?

25. How can oxycellulose be formed on a cotton sheet? How can it be detected in a qualitative way? in a quantitative way?

26. Name three classes of chemical compounds used for producing a variety of finishes on cotton goods. How are they applied?

27. Give an example of a quaternary ammonium salt used for making cotton water-repellent.

28. How are the melamine resins made and used? Are these resins thermosetting or thermoplastic? What is meant by methylolmelamine?

8 · Rayon

Rayon fabrics and knit goods have become so widely used that the world's consumption of rayon filament and staple fiber is second only to that of cotton. Rayon is by far the most important manufactured textile fiber. During its development to this enviable position among textile fibers, it has been designated by various names, such as artificial silk, wood silk, fiber silk, and art silk. The implication in these names is that it is a substitute for silk (as it was originally intended to be). The silk manufacturers frowned on the use of these names, and a point was reached when the rayon manufacturers felt that they had a product that could stand on its own merits without the help of the word silk. The result was that, in 1924, in the United States, groups of retailers and manufacturers sought a different and standardized name for this product, and the word rayon was proposed. In 1937, the Federal Trade Commission published its Rayon Trade Practice Rules, which became law in the same year. We are especially interested in two of these rules, (1) the definition of rayon, and (2) the matter of brand names attached to goods made from rayon.

The official definition of rayon under this law is essentially as follows: the word rayon is a generic term for manufactured fibers or yarns produced chemically from cellulose, or with a cellulose base, and for threads, strands, or fabrics made therefrom, regardless of the process used in the manufacture of such fibers, yarns, or goods.

Furthermore, in order to promote fair practice and competition and protect the buying public, brand names must have the word rayon attached, as, for example, Acele rayon, Crown rayon, Bemberg rayon, Celanese rayon, etc.

The British have proposed a definition for rayon which causes some confusion. This definition[1] says that rayon is a generic term applied to all fibers for textile use which are not of natural occurrence. It is seen that the American plan confines the use of the word rayon to fibers made from cellulosic materials, whereas the British plan would include all man-made textile fibers such as nylon, Vinyon, Velon, and Lanital.

The development of rayon since the start of the century has been a hard struggle. Even though it started as a potential competitor of silk, rayon was so inferior to silk that no one thought it would ever be taken very seriously. It was much too weak, and when wet it lost most of its strength and would not withstand laundering. It was too bright and lustrous, and had an undesirable glare. It was so stiff that fabrics made from it would not drape. The fabrics would shrink badly and unevenly, and it was almost impossible to dye them uniformly in light colors. And yet, in spite of all these defects, the many men back of rayon persisted and struggled against all sorts of prejudices and physical and mechanical difficulties. They knew their product had to be improved, so they set about improving it. Chemical researches were instituted; new machinery was developed; new and better controls were established; every effort was made to standardize all the operations in the manufacture of rayon; time, temperature, speed of machinery, pressure, humidity, and many other conditions were put under rigid control. What have been the results? Today rayon is one of the most uniform and reproducible filaments in the textile industry. It dyes more uniformly than natural fibers; it shrinks evenly and very little; the luster can be controlled at will, and the decrease in strength when wet is not too great.

Today rayons can be laundered satisfactorily, and we find that fabrics made from rayon have draping qualities excelled by none of the other textiles. Furthermore, we have high-tenacity rayons, with a tensile strength greater than steel, which are used in cord fabrics for heavy-duty truck tires and are superior to any previously used fibers. Not only is rayon being made in the long continuous filament form, but it is being furnished in a staple form (from 1.5 to 6 in. long) which can be blended with cotton and wool. In other words, rayon has arrived. The figures speak for themselves. In 1946 about 950,000,000 lb of rayon were produced in the United States. This means that the production and use of rayon in this country is exceeded only by cotton. That is, from the volume standpoint, rayon is the second most important textile fiber.

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[1] *J. Textile Inst.*, **35**, P28 (1944).

The earliest patent for the manufacture of fine threads was granted to a Swiss chemist, George Audemars, in 1855. Twenty-two years later Sir Joseph Swan in England produced fine filaments by forcing nitrocellulose solutions through small orifices.

However, the man who is recognized as the father of rayon is Count Hilaire de Chardonnet, who was the first one to produce artificial silk on a commercial scale. Chardonnet nitrated cotton with a mixture of concentrated HNO_3 and H_2SO_4 and then dissolved the cellulose nitrate in a mixture of alcohol and ether. This solution was forced through a spinneret into a chamber through which warm air was passed. The warm air evaporated the solvent so that fine filaments of cellulose nitrate were left. They were later denitrated with ammonium sulfide. Chardonnet took out his first patents in France in 1884, and in 1891 started the manufacture of artificial silk at Besançon at the rate of 100 lb per day. (Compare this with the production of a single plant in this country which makes 100,000,000 miles of filament each day.) The business struggled for a few years, and then in 1900 Chardonnet silk was exhibited at the Paris Exhibition. Dividends increased immediately, and in 1905 a 60% dividend was declared. Meanwhile Cross and Bevan had discovered viscose, which could be made at a lower cost, and the doom of Chardonnet's rayon was sealed. This particular rayon was sold under such names as Chardonnet silk, Tubize silk, nitro silk, and chardonize. It was manufactured in the United States at Hopewell, Va., but never became a very important factor in the American rayon industry and is no longer being made.

In 1910, Courtaulds of England came to the United States and organized what is now the American Viscose Corporation, which makes almost one-half the total rayon manufactured in this country. In 1921 the du Pont Company entered the field, and in 1925 Industrial Rayon Corporation started production. At that time all these companies were making rayon by the viscose process. In 1921 another British company built a plant in this country and started to manufacture an acetate rayon, Celanese. This company is now known as the Celanese Corporation of

America and is one of the recognized leaders in the field of acetate rayon.

At the present time only three kinds of rayon are being manufactured, cuprammonium, viscose, and acetate. That is, there are three fundamentally different processes by which rayon is made. All manufacturers of viscose rayon, for example, use the same general procedures, but each has his own specialized controls, which he feels make possible the reproducing of his product day after day. Perhaps rayon's outstanding feature is its reproducibility. It is impossible for a cotton spinner to turn out exactly the same yarn each day, because his raw material is not constant. But in the rayon industry filaments of identical fineness, luster, and strength can be produced continuously. This is the difference between man and nature. Man's processes, tests, and machinery are not subject to weather, heat, cold, humidity, soil, rain, etc., but natural fibers are affected by these things.

In the early days rayon was called artificial silk and was supposed to take the place of silk for some purposes. It did not replace silk, nor did it cause the consumption of silk to decrease. In fact, it probably stimulated the use of silk. At any rate, the consumption of silk in the United States was doubled during the 20 years preceding 1940. Thus we see that rayon is not a substitute for, nor a competitor of, silk. It is simply a new textile fiber which has been developed to fill a unique place in the field of textiles. Its acceptance has been so widespread that, during the same 20 years in which the consumption of silk was doubled, the production of rayon increased almost 40 times.

Most of the product is the continuous filament, but within recent years there has been an increasing demand for rayon staple fiber. Regular rayon is twisted like silk to make yarns with the desired denier, but staple fiber is spun like cotton and wool to make spun rayon fabrics. Staple fiber can also be blended with wool or cotton before spinning to make mixed yarns.

In addition to the rayon made by the three processes and in filament or staple fiber form, it is also classified according to various factors connected with its use. For example, some are bright and others dull; some have regular strength, whereas others have a high tenacity; still others have a high impact resistance, crimped fiber, etc.

The American manufacturers of rayon are not very numerous.

TABLE 34

VISCOSE MANUFACTURERS AND BRANDS

Manufacturer	Brands				
	Filament		Staple Fiber		
	Regular	High-Tenacity	Regular	High-Tenacity	Crimped
American Enka Corp.	Briglo Englo Perglo	Tempra Vitala			
American Viscose Corp.	Chalkele Crown Dulesco	Rayflex Tenasco	Fibro	Avisco	Auricon
Delaware Rayon Co.	Delray Delustra				
E. I. du Pont de Nemours & Co.	du Pont	Cordura Fiber G			
Hartford Rayon Corp.	Belastraw Hartford				
Industrial Rayon Corp.	Dul-tone Premier Spun-Black Spun-Lo	Tyron			
National Rayon Co.	National				
New Bedford Rayon Corp.	Newbray Newdull Newglow				
North American Rayon Corp.	North American Xtra-Dul	High Narco Super Narco			
Skenandoa Rayon Corp.	Skenandoa Veri-Dul				
Tubize Corp.	Chardonize Tubize	Hygram			

Tables 34, 35, and 36 list these manufacturers, with the type of rayon they make, together with the special brand names for their products.

Single rayon filaments and yarns are numbered by the denier system (page 102) so that the smaller the denier, the finer the filament or yarn. (Spun rayon yarns are numbered like cotton yarns.) When yarns are being described, two numbers are used, one for the denier of the yarn and the other for the number of filaments in the yarn. For example, 65/45 means that 45 individual filaments have been twisted to make a yarn that is 65 denier.

TABLE 35

Acetate Manufacturers and Brands

	Brands		
Manufacturer	Regular	High-Tenacity	Staple Fiber
American Viscose Corp.	Seraceta		Seraceta Fibro
Celanese Corp.	Celanese	Fortisan	Celairese Lanese
E. I. du Pont de Nemours	Acele		Acele
Tennessee Eastman Corp.	Eastman Acetate Koda		Teca
Tubize Corp.	Chacelon		

TABLE 36

Cuprammonium Manufacturers and Brands

American Bemberg Corp.	Aristocrat Bemberg Matesa Snowkrepe Star Breeze

To make such a yarn, the denier of each filament would have to be about 1.5, but in 35/60 rayon yarn the single filament would be about 0.5 denier. Single filaments of rayon can be produced over a wide range of denier, from 0.5, which is much finer than natural silk, to 5.5, which is coarser than horsehair.

The Cuprammonium Process

From the standpoint of volume of production, the cuprammonium process is the least important one used for making rayon because it accounts for only about 5% of the rayon made in the

United States. However, it has the distinction of producing finer filaments than any of the other rayon manufacturing processes. Where yarns composed of such fine filaments are required, this rayon is greatly prized.

The cuprammonium process was developed in Germany. The first patents were taken out by Fremey and Urban in 1897, and the Glanzstoff Company in Germany was the first large-scale commercial producer. Later the I. P. Bemberg Company gained control of the business and came to this country in 1926 to build a plant for making rayon by this process. It was known by such names as Glanzstoff, cuprate silk, copper silk, Pauly silk, and cuprammonium silk, but today it is most generally designated as Bemberg rayon.

In the cuprammonium process, cotton is dissolved in Schweitzer's reagent, and the solution is forced through spinnerets (the spinning operation) and coagulated in an acid bath. The word spin or spinning, when used in connection with man-made filaments, refers to the operation in which solutions or molten solids are extruded through minute orifices to form fine streams of liquid, which may then be solidified or coagulated, depending on what process is being used. Recall that Schweitzer's reagent is an ammoniacal solution of copper hydroxide and may be made by dissolving copper hydroxide in ammonium hydroxide. The present cuprammonium process makes this reagent in a novel way in the presence of cotton linters. Concentrated solutions of $CuSO_4$ and NaOH are mixed to form $Cu(OH)_2$.

$$CuSO_4 + 2NaOH = Cu(OH)_2 + Na_2SO_4$$

The $Cu(OH)_2$ is precipitated in a finely divided semigelatinous form. Highly purified cotton in the form of linters is added and thoroughly mixed. The result is that all the small fibers are wetted with $Cu(OH)_2$.

The excess liquid is pressed out, and the solid mass is washed with water until all the Na_2SO_4 has been removed. The $Cu(OH)_2$, being insoluble, is left on the cotton fibers. The mass is then pressed until it retains only about 40% water. It is then squeezed through a sieve and at the same time deaerated with a vacuum. Deaeration is necessary because cellulose, when in contact with Schweitzer's reagent, is very sensitive to oxidation, even by such a weak oxidizing agent as air. Note that we now have a very intimate mixture of cotton fibers and copper hydroxide, each fiber being impregnated with $Cu(OH)_2$. This mass is then mixed with NH_4OH for 24 hours. The NH_4OH reacts with $Cu(OH)_2$ and makes Schweitzer's reagent. Note that this happens at the immediate surface of each fiber, so that the maximum efficiency of solvent action is obtained. By this method it is possible to obtain an 8% solution of cellulose in Schweitzer's reagent.

The thick solution is spun by the Thiele stretch-spinning process, in which the fine streams of solution, after extrusions, pass downward through a long hollow tube with a stream of water flowing in the same direction. As water is a weak coagulant, the filaments will be partially coagulated and in this plastic stage will be stretched by the motion of the water. This stretching produces a finer filament and also accomplishes some orientation of the cellulose molecules. The filaments are then further coagulated and hardened by passing through an acid bath, and are finally washed and wound on bobbins.

The original special feature and advantage of Bemberg rayon was its small denier. It was possible, by the proper control of the temperature and the relation between speed of extrusion and rate of flow of water, to obtain exceptionally fine filaments. These filaments could be made as fine as those of real silk, which at that time was quite an accomplishment. However, such refinements in technique have been made that it is now possible to produce any of the rayons in deniers smaller than real silk.

The Bemberg Company is producing regular yarns from 35 to 200 denier in which the singles are from 1.2 to 1.3 denier each. They also make a superfine yarn from filaments of 1 denier. These yarns range from 25 to 100 denier. A still finer yarn, 30/74, is also made.

Cuprammonium rayon resembles viscose in many of its physical properties. Its dry tenacity is about the same (1.7 to 2.3 gm/denier), but its wet strength is somewhat higher (0.95 to 1.3). The elongation at the breaking point is about the same. In the dry state it will stretch from 10 to 17% before it breaks, and when wet it breaks after a stretch of 17 to 35%. Its normal regain at 65% R.H. is 11%, and at 95% R.H. is 27%. The tensile strength is similar to that of regular acetate rayon, about 23,000 psi. The specific gravity is 1.54.

Note that this type of rayon is a regenerated cellulose. It is cellulose that has been put into solution and then taken out of solution, but in this regenerated form the arrangement of molecules is entirely different. It is certainly a modified cellulose, and usually a degraded cellulose with shorter chains caused by unavoidable oxidation. It should therefore be more active and more easily attacked by all chemical reagents, but the type of reaction will be the same as shown by cotton. It is merely a matter of degree.

The Viscose Process

The steps in the viscose process can be briefly stated as follows: cellulose is mercerized with NaOH and then xanthated with CS_2, after which it is dissolved in NaOH to form a spinning solution, from which cellulose is regenerated by the action of acid. Thus viscose rayon is a regenerated form of cellulose which should have chemical properties about the same as cotton, but should exhibit different physical properties. The most logical assumption is that when cellulose is regenerated there will be an entirely different orientation of molecular chains, and thus a different proportion of cyrstalline and amorphous portions. This factor will be emphasized in the following discussion of physical properties.

PHYSICAL PROPERTIES OF VISCOSE RAYON

Viscose rayon will absorb more water from the atmosphere than cotton will, and the American Society for Testing Materials has set a figure of 11% for the regain, at 70° F and 65% R.H. As would be expected, the percentage of moisture in viscose rayon will vary with the humidity of the atmosphere to which it is exposed. For example, at a R.H. of 30% the moisture content is about 7.5%, at 50% R.H. it is 10.5%, and at 80% R.H. it is 17%. The increased moisture absorption of viscose is attributed to the amorphous portions of the regenerated cellulose as compared with native cotton.

The strength of viscose rayon can be varied over a considerable range, depending on different manufacturing techniques, most important of which is the amount of stretching to which the filaments are subjected. One of the chief objections to rayon has been its low strength when wet; e.g., viscose rayon loses almost half its tenacity when it is wet. Thus, the dry strength of ordinary viscose runs from 1.8 to 2.2 gm/denier, but the wet strength is much less. We shall find, however, that improved types of viscose are considerably stronger. This is due to a more uniform orientation of the molecular chains in the regenerated cellulose. This increased orientation leads to increased tenacity. It is common knowledge that rayon fabrics must be handled carefully when they are wet, and this of course is because of the lower wet strength, but it must be pointed out that if rayon is wetted and then allowed to dry, the original dry strength is regained. However, if a rayon fabric is distorted while wet, it will not assume its original shape when it dries.

Elongation is another important physical property of rayon which is definitely associated with the relative amount of orientation of molecular chains. The per cent elongation is the percentage which a fiber or filament can be stretched before it breaks. The magnitude of elongation is dependent on, and varies with, two factors, namely, orientation and moisture. Ordinary dry viscose filaments have elongations of 11 to 21%, but when these same filaments are wet they can be stretched between 20 and 35% before they break. Between the two extremes of dry and wet we should expect to find rayon more easily stretched at higher relative humidities. This is found to be the fact, and so rayon curtains, dresses, etc., go out of shape during use in atmospheres of high humidity. We have just learned that increased orientation results in increased tenacity, but the opposite is true of elongation. Whereas ordinary viscose can be elongated 11 to 21%, highly oriented filaments (high tenacity) can be stretched only about 6 to 12%. However, the effect of moisture is in the same direction; that is, when wet these same strong filaments will stretch 13 to 20%.

We found some interesting facts about the elasticity of fibers in Chapter 5 (see pages 110–116). Perhaps these pages should be reread at this time. If viscose is stretched about 4% and then the stretching load is removed, the yarn will contract rapidly so as to lose about 55 to 60% of the induced length, that is, 55 to 60% of the 4% elongation. Then, if the yarn is allowed to stand, a very slow further contraction will occur, and this creep will continue until the original unstretched length is almost reached. Now let us examine the behavior of the viscose yarn when it is subjected to stretching. If a load equal to the strength of the yarn is applied, the yarn will break. But suppose the load is only one-third or one-half as great. Then the truly elastic property of the rayon will cause it to be elongated quite rapidly. However, if the load is retained, there will be a further elongation, but this will take place very slowly. It is thought that the rapid elongation is a measure of the real elastic property of rayon, but that the slow stretching is due to the plastic-flow property of rayon. Thus we find that rayon can creep in both directions; that is, a slow creeping elongation follows the initial rapid stretching, and conversely, a slow creeping recovery follows the first rapid snapback when a stretching load is removed. Both the slow stretching and slow recovery become more significant at higher humidities. The user of rayon fabrics will find many of their faults explained by this property of creep.

CHEMICAL PROPERTIES OF VISCOSE RAYON

It is well known that most regenerated rayon goods must be handled more carefully than cotton. One of the main reasons for this is rayon's high absorbency of water. If viscose is oven-dried it is found to be a very good drying agent and will remove water from other substances. The absorption of water is accompanied by considerable swelling, up to about 7% axial swelling. The name regenerated rayon tells us that such rayon is really cellulose in some sort of regenerated form, and that its chemical properties should be similar to those of cotton, but its physical properties may differ. Thus we find that rayon has the properties of cotton, but to a greater degree, and that rayon is more easily attacked by any aqueous solution, because it swells when wet.

For example, viscose is more easily hydrolyzed by dilute acids to form hydrocellulose (see page 133). When rayon is subjected to any acid treatment, intelligent attention must be paid to such factors as concentration, temperature, and time of contact. Organic acids, such as dilute acetic acid, can be used with safety even at fairly high temperatures, but inorganic acids must be used in quite dilute solutions and at temperatures only slightly above room temperature.

The effect of oxidizing agents on regenerated rayon is similar to their effect on cotton. Oxycellulose (see page 134) is formed and the filaments are weakened, the loss in strength depending on the extent of oxidation. It is fortunate that it is unnecessary to bleach most rayon goods. However, if it becomes necessary, bleaching should be done with slightly alkaline sodium hypochlorite solutions at room temperature.

Regenerated rayon is more sensitive than cotton to dry heat. The result is a material with a higher copper number and increased alkali solubility, both of which show that degradation has taken place.

STEPS IN THE VISCOSE PROCESS

From the standpoint of volume of production, this is the most important process for making rayon, because about 70% of the world's rayon consumption is viscose rayon. It is made in continuous filament and staple fiber in all the principal countries of the world, and the larger manufacturers are also making it in regular and high-tenacity qualities. In 1892 Cross and Bevan, in England, discovered that cellulose could be put into alkaline solution by treating it with NaOH and CS_2, and that the cellulose could be regenerated by acidifying the solution. This was the beginning of viscose rayon, the use of which has increased so much that today about 600,000,000 lb of it are produced in the United States each year. The production of textile filaments by the viscose process was developed in England by Courtaulds, Ltd., and in Germany in the plants of Donnersmark in Stettin and Glanzstoff in Elberfeld. The American Viscose Corporation is an outgrowth of Courtaulds. It was the first company to manufacture rayon in this country, and in 1910 it produced 1,000,000 lb of viscose rayon out of a total world production of 17,000,000 lb. One of the main reasons for the phenomenal increase in the production of viscose rayon is its much lower cost as compared with the other rayons.

The reader should refer to the chemistry of the viscose reactions as discussed in Chapter 6, pages 155–160. There are nine steps in the viscose process: (1) steeping, (2) shredding, (3) aging, (4) xanthation, (5) preparation of spinning solution, (6) ripening, (7) filtration, (8) spinning, and (9) purification.

(1) STEEPING

The raw material from which viscose is made is high-grade sulfite wood pulp which is delivered to the mill in large sheets. These sheets are immersed in 18% NaOH which is of mercerizing strength, and therefore considerable swelling of the cellulose will take place. The product of this reaction is known as alkali cellulose. After the pulp has been thoroughly impregnated, the material is subjected to very high pressure with a hydraulic ram. The object of this is to press out excess liquid until the material weighs three times as much as the original pulp.

(2) SHREDDING

The sheets of alkali cellulose are transferred to a shredding machine which crumbles them and tears and pulls them apart, but does not grind them. The machine is provided with a jacket through which water can be circulated so as to control the temperature and keep it about 20° C. In all the steps in the viscose process, the maintenance of the proper temperature is very important. The alkali cellulose is left in this shredder until the sheets are converted into a light fluffy mass having the consistency of crumbs.

(3) AGING

The crumbs are then transferred to steel containers in which they are stored from 48 to 72 hours under controlled temperature conditions between 21° and 23° C. The temperature during the aging of alkali cellulose seems to be quite important. During this time considerable degradation takes place due to the oxidative effect of air on cellulose in the presence of alkali. This is really desirable because it causes a chain shortening which lowers the viscosity of the xanthate solution to be spun later. If this were not done the solution would be too viscous to spin.

(4) XANTHATION

The aged crumbs are then transferred to large rotating churns or drums and CS_2 is added slowly until it equals 30 to 40% of the weight of the original wood pulp. The formation of cellulose xanthate is accompanied by some rise in temperature, which must be avoided. Therefore the drums are cooled with water so as to keep the temperature below 30° C. The drums are rotated until the crumbs become orange-colored all the way through. This is an indication that the chemical reaction is complete. Alkali cellulose has now been converted into cellulose xanthate.

(5) PREPARATION OF SPINNING SOLUTION

Cellulose xanthate is fairly soluble in water but more easily soluble in dilute NaOH, and the next step in the process is the preparation of a solution of cellulose xanthate which can be extruded into filaments. To do this the temperature is reduced to 17° C, and a dilute solution of NaOH is added in such an amount that the charge will contain about 6.5% NaOH and 7.5% cellulose in the form of xanthate. This operation requires from 3 to 6 hours, and during this time the xanthate dissolves to give a thick, viscous, orange solution known as viscose. During this operation, the final degree of dullness of filaments is determined. If a bright lustrous yarn is to be made, nothing need be added to this solution, but if a dull matte yarn is desired, certain mineral pigments are added at this time. The amount of such pigments will determine the dullness of the final yarns.

(6) RIPENING

Before the spinning solution is in the proper condition for spinning, it must be allowed to stand for some time. During this ripening period chemical changes take place (page 158) which determine the spinning quality of the solution. The ripening time is usually four to five days, with the temperature controlled between 15° and 20° C.

(7) FILTRATION

At this time there are some insoluble impurities which must be removed, and so the spinning solution is pumped through several filters and at the same time deaerated with a vacuum to remove all air bubbles. If insoluble particles are left in the spinning solution, the openings in spinnerets become clogged when the solution is spun. The presence of small air bubbles in the solution would cause weak spots in the final yarns.

(8) SPINNING

In this step the final filaments and yarns are formed, so that it is perhaps the most important step. The spinning solution is pumped under uniform pressure through spinnerets into an acid coagulating or hardening bath. A spinneret is a cap or jet, smaller than a dime, provided with a number of fine, funnel-shaped openings so small as to be almost invisible. Spinnerets are made of precious metals such as platinum, platinum-gold, platinum-iridium, or tantalum. The filaments made by one spinneret will be twisted into one yarn. Each orifice forms an individual filament, and so the size and number of the orifices determine the number of filaments in the final yarn, and its denier. A single spinning machine comprises numerous spinnerets, all of them immersed in a long trough through which the coagulating solution flows. The function of the coagulating bath is two-fold. It regenerates and coagulates the cellulose, and it separates and decomposes soluble by-products arising from carbon disulfide. As the streams of cellulose xanthate solution leave the spinneret under the surface of the acid bath, they are coagulated and hardened. They are then pulled under a guide, up and around a glass feed wheel, and then down through a small funnel and into a rapidly revolving bucket or pot. As the yarn enters the bucket, it is thrown to the side by the centrifugal motion, and this imparts a certain amount of twist to the yarn and also gives it some stretch which will increase its strength. As the spinning continues, the yarn forms a cake on the inside of the bucket.

(9) PURIFICATION

The cakes are washed with dilute sodium sulfide solution to remove residual sulfur. This is usually done at about 50° C, after which the yarn is washed thoroughly and then bleached with hypochlorite bleach liquor at room temperature. Small amounts of residual bleach are removed by an anti-chlor, after which the yarn is well rinsed and dried.

At two points during the manufacture of viscose the cellulose is degraded. Heuser and Shuster[2] showed that during the first ten hours of aging, the viscosity drops to less than one-third of its original value, but after 10 hours the change is increasingly slower. They also found that the viscosity drops during xanthation. In the first seven hours of xanthation, the viscosity dropped an amount equal to about one-third the value at the start of xanthation. There is practically no further change during the ripening period.

Commercial viscose yarns run from 50 to as high as 900 denier, depending on their intended use. Single filaments run from 1.0 to 5.5 denier, with 1.5 to 2 denier filaments being most widely

[2] *Cellulosechemie*, **7**, 19 (1926).

used for all types of fabrics. Fine viscose filaments of 0.5 denier have been made and used for various sheers.

HIGH-TENACITY VISCOSE RAYON

The manufacturers have used every effort to improve the quality of rayon since it was first put on the market, and one of their chief aims has been to increase its strength. The advent of World War II stimulated these efforts, with the result that we now have high-tenacity viscose rayon with tenacities ranging from 3.6 to 5.0 gm/denier, which is about the same as degummed silk. This high-tenacity rayon is made from highly purified cotton instead of wood pulp, and the most rigid controls are imposed during its manufacture. It is made by the viscose process, but the high strength is obtained by a special type of spinning accompanied by an extra amount of stretching. The stretching has two effects: it lines up the molecular chains of cellulose in a more nearly parallel manner, that is, a higher degree of orientation; and it transforms a large number of amorphous areas into a more rigid crystalline state. These two results are closely connected. The amorphous portions of cellulose are easily swollen and hence easily deformed by any physical stress. On the other hand, the crystalline portions of cellulose are more highly oriented with parallel chains, so that these chains can be held together by hydrogen bonds and polar forces. This means that such portions will be stronger and less easily deformed.

However, we have learned that these same conditions that produce the advantage of increased strength will reduce the flexibility of a filament. This is closely connected with the property of softness and is reflected in the elongation of the filament. Table 37 shows the tenacity and per cent elongation of three types of viscose rayon. It shows that, wet or dry, the elongation decreases as the strength increases.

TABLE 37

TENACITY AND ELONGATION OF VISCOSE RAYON

	Tenacity, Dry, gm/denier	Tenacity, Wet, gm/denier	Elongation at the Break	
			Dry	Wet
Regular	1.5–2.4	0.7–1.0	15–20%	20–35%
Medium-tenacity	2.4–3.0	1.2–1.7	12–20%	17–30%
High-tenacity	3.0–4.6	1.9–3.0	9–16%	14–20%

High-tenacity viscose filaments can be produced in small deniers so that yarns made from them will be very strong and yet fine. These yarns are used wherever such a combination of strength and fineness is desired. One of their most important uses is in cord fabrics for heavy-duty truck tires. It has been found that tires made with high-tenacity viscose rayon cords will stand more punishment from sudden impact and high temperature and will give more mileage than any other cords. Most of the high-tenacity viscose yarns are sold in 1100 to 1200 denier sizes.

Ten well-known high-tenacity viscose rayons are manufactured by the following companies:

American Enka Corp.	Tempra and Vitala
American Viscose Corp.	Rayflex and Tenasco
Courtaulds (England)	Durafil
E. I. du Pont de Nemours & Co.	Cordura
Industrial Rayon Corp.	Tyron
North American Rayon Corp.	High Narco and Super Narco
Tubize Corp.	Hygram

The du Pont Company is developing a high-tenacity viscose which is called Fiber G. It is said to be stronger than any of the others and has the added advantage of a wet strength that is 75% of the dry strength. It has been produced in 240/120 and 1100/480 yarns.

DELUSTERING RAYON

The control of luster in rayon is interesting. We know that viscose is a clear, colorless, transparent substance (cellophane is a film form of viscose). Luster is the reflection of light from a smooth surface, but if the substance is transparent, most of the light will be transmitted and not reflected. If a material like a yarn is composed of numerous transparent filaments, the light that passes through one filament will strike another, part of it being reflected. This continues throughout the yarn, each filament reflecting light which was either directed on it or transmitted to it from other filaments. But since all of the filaments have the same index of refraction there will be very little scattering of the light reflected from the yarn, and we say that it has a high luster.

One of the early problems encountered in the rayon industry was this one of glare or luster, and how to dull it. The first thought was to roughen the surface of the filaments so they would be more like ground glass. This was accomplished by various modifications in the spinning operation. When a stream of liquid is coagulated, the first effect must be on the outside, and as hardening begins, the outside must harden first. This suggests that in the early stages of regeneration, the picture of a viscose filament is a sort of hardening skin enclosing a soft, semigelatinous, not yet completely coagulated mass. Preston[3] demonstrated that a defect in rayon, known as milkiness, was caused by this outer skin breaking away from the interior, leaving a pocket. Assuming that the interior of the filament is still a solution containing only about 7% NaOH, what would happen if the coagulating bath were made quite concentrated by the addition of electrolytes or sugar? The outer skin of the filament would act as a semipermeable membrane (an osmotic membrane) separating the dilute solution inside the filament from the stronger solution outside. Water would move from the dilute solution through the membrane to the stronger solution. The result would be a shrinkage in the volume of the interior of the filament (a decrease in the cross-section area of the interior). The skin could adapt itself to this shrunken interior only by collapsing and the result would be an irregular cross-section area, or a more or less serrated filament. This dulled the luster somewhat, but probably its main advantage was the reducing of slippage of yarns. Smooth, round yarns slip past each other easily, but if their surfaces are roughened the tendency to slip is reduced.

The method for dulling used at present is to embed in the filaments some finely divided foreign material which has a very different refractive index from the filament itself. Various inorganic pigments have been used for this purpose. They must of course be colorless and unaffected by acids, alkalies, and bleaching agents. The one most widely used for this purpose is titanium oxide, a white pigment used in some of the better-grade white paints. Because of its high index of refraction, it is about a thousand times as effective as zinc oxide.

A new method[4] has been proposed for delustering viscose rayon in which quaternary ammonium hydroxides, such as trimethyl benzyl ammonium hydroxide (Triton B), are incorporated with the viscose solution before it is spun. The solution is then coagulated rapidly before regeneration of cellulose begins. The yarns are then stretched about 125% and regenerated with heat. The result is a rayon with a dull, rough, finely crenulated surface.

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[3] *J. Soc. Chem. Ind.*, **50**, T199 (1931).

[4] Cramer, U.S. Patent 2,412,969 (1946).

CRIMP IN RAYON

There are certain uses for rayon in which a crimp or waviness is desirable. This is especially true of staple rayon (page 236), which may be mixed with cotton or wool, because the crimp gives it better spinning quality and yields a loftier yarn which will cover better. Some crimped rayons having a somewhat wool-like quality were used extensively during the wool shortage in World War II.

The usual method for making rayon yields a straight filament, so that the introduction of crimp must be accomplished by mechanical or chemical means, usually the former. One mechanical method for imparting crimp to yarn is to twist it tightly while wet and then set it with steam. After the twisted yarn is cooled and dried, it is untwisted. This unnatural crimp is not permanent, because, after the tension imposed by tight twisting, the creep factor will become operative, and a general straightening occurs. Some rayons are crimped by passing them between hot fluted rollers. Other methods involve modifications of the usual extrusion and coagulating technique. An example of such methods is divulged in a patent[5] assigned to du Pont. According to this patent, viscose filaments are extruded into a coagulating bath which coagulates rapidly before any regeneration of the cellulose takes place. Thus a careful adjustment of the relative speeds of extrusion and the drawing-off of the regenerated filaments is maintained. It is extruded about four times as fast as it is drawn off.

The Cellulose Acetate Process

Acetate rayon is the baby of the rayons, dating only from about 1924, but it has graduated from its swaddling clothes and is now in long pants. About 32% of the rayon produced is made by this process.

Cross and Bevan in England were the first ones to develop a good process for making cellulose acetate in industrial quantities. This was in 1894. In 1898 Donnersmark in Stettin started the production of cellulose acetate. The early production of cellulose acetate was not pointed toward the formation of a filament. It was found that this compound could be dissolved in certain solvents like chloroform and used as a protective coating for cloths and metals. During World War I it was used as a "dope" for fabrics and airplane wings. In 1913 some English businessmen brought the Dreyfus brothers from Basle, Switzerland, to England, and in 1918 the British Cellulose and Chemical Manufacturing Company was in operation at Spondon. This later became British Celanese, Ltd., which is responsible for the remarkable development of acetate rayon, so much so that the name Celanese is largely associated with it, even though several other brands of acetate rayon are on the market. The British Celanese firm came to the United States and built a plant at Amcelle, Md. This company later became the Celanese Corporation of America.

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[5] Underwood, U.S. Patent 2,413,123 (1946).

Acetate rayon is soft and silky, with a suppleness that makes it prized for certain types of fabrics. It is inherently resistant to wrinkling and creasing and is very little affected by perspiration. It must be dyed by special kinds of dyes that do not color wool or cotton (or at least will dye them only in light shades), and therefore it is possible to obtain cross-dyed effects when mixtures of acetate and other fibers are dyed. Acetate rayon is somewhat thermoplastic, so that it requires care in ironing. However, this property may be used for obtaining certain permanent effects in finishing acetate fabrics.

At present there are five companies in the United States making acetate rayon under the following trade names:

American Viscose Corp.	Seraceta
Celanese Corp.	Celanese
E. I. du Pont de Nemours & Co.	Acele
Tennessee Eastman Corp.	Eastman Acetate and Koda
Tubize Corp.	Chacelon

Before discussing the actual manufacture of acetate rayon, let us see what we are dealing with and what factors determine manufacturing techniques and quality of product. Acetate rayon is made by dissolving cellulose acetate in acetone and extruding this solution through a spinneret downward against a rising flow of warm air. The warm air evaporates the acetone, leaving the acetate in the form of a long continuous filament.

Cellulose acetate is made by acetylation of cotton linters with acetic anhydride. Recall that cellulose has three alcoholic OH groups in each anhydroglucose unit (page 125). If it is acetylated completely, the product will be a triacetate with an acetyl constant of 44.8%. If it is acetylated so that an average of two of the three OH groups is esterified (a diacetate), the acetyl content is 35.0% and the monoacetate is 21.1% acetyl. The triacetate is not suitable for making filaments for two important reasons: (1) there is no cheap solvent which can be used for preparing a spinning solution, and (2) filaments with such a high acetyl content are too stiff, hard, and wiry. The best acetate for making rayon has from 36 to 41% acetyl groups in it.

The importance and effect of the acetyl content are shown by the following relationships. The higher the acetyl content, the lower the viscosity of the spinning solution. However, one can vary the viscosity of the solutions containing the same amount of acetyl by properly controlling various factors during the manufacture of rayon. A higher acetyl content yields a stiffer and more wiry filament, whereas acetates of lower acetyl content yield filaments that are softer and more pliable. Rayon made from acetate with higher acetyl content will have a little higher melting point. Each manufacturer works out his own process and controls, and obtains an amazing degree of uniformity and reproducibility.

One might think that methods could be found by which cotton could be acetylated to from 35 to 41% acetyl, and would then be ready to dissolve and be spun. However, it appears that a satisfactory filament-forming acetate depends not only on the content of acetyl groups but also on their distribution. Miles (page 154) discovered that a satisfactory acetate could be made by acetylating cellulose completely and then hydrolyzing off some of the acetyl groups. The acetate would then be soluble in acetone, a cheap solvent. Cramer and Purves[6] suggest that, if cotton is acetylated to 38% acetyl content, too many alcohol 6 groups are blocked, but if it is completely acetylated and then partially hydrolyzed, the proportion of free alcohol 6 groups is greater, and for that reason the acetone solubility is satisfactory. Therefore, we must acetylate cotton completely and then deacetylate to the point where the acetate will be soluble in acetone and will yield a soft, flexible filament.

[6] *J. Am. Chem. Soc.*, **61**, 3458 (1939).

There are six steps in the manufacture of acetate rayon: (1) swelling pretreatment, (2) acetylation, (3) partial hydrolysis, (4) precipitation, (5) preparation of spinning solution, and (6) spinning.

(1) PRETREATMENT

The raw material for making acetate rayon is cotton linters, which is purified by kier-boiling. During the first step in the process, the cotton fibers are impregnated with a swelling agent. This is usually glacial acetic acid containing a small amount of concentrated H_2SO_4. Acetic acid alone acts as a swelling agent, but if some compound such as H_2SO_4 or $ZnCl_2$ is present, it acts as an activator because it will attack the surfaces of the cotton fibers and peptize them. Thus in this first step the cotton fibers are opened up so that the action of the acetylating agent will be more efficient, and the surfaces of the fibers are activated. One hundred parts cotton linters containing 5 to 6% moisture are added to 400 parts glacial acetic acid containing 10 parts H_2SO_4. This is done in portions, and the temperature is not allowed to rise above 20° C in this step. This prevents excessive hydrolysis of the cellulose.

(2) ACETYLATION

This is accomplished by the action of acetic anhydride in the presence of a catalyst and a diluent. The catalyst and diluent are already present, so that all that is necessary is to add 400 parts acetic anhydride with efficient mixing. During the first two hours the temperature is kept at 20° C, but after that it is allowed to rise. After a short time the cotton fibers begin to soften and lose their fibrous form, and finally are completely dissolved.

(3) PARTIAL HYDROLYSIS

One hundred and twenty parts of 50% acetic acid are thoroughly mixed with the viscous solution of cellulose acetate in acetic acid and allowed to age for 12 to 16 hours at 50° C. During this time the acetone-insoluble primary acetate is converted into the secondary acetate, which is soluble in acetone. The control of dilution and temperature during this partial hydrolysis determines the properties of the final product. Each manufacturer adjusts his conditions so that he will produce a filament with properties suitable for the purpose for which it is to be used.

(4) PRECIPITATION

This step is quite simple. It consists of running the cellulose acetate solution in fine streams into water which is vigorously stirred. The acetate is precipitated in white flakes, which are thoroughly washed and dried.

(5) PREPARATION OF SPINNING SOLUTION

The white flakes of secondary acetate are dissolved in acetone to form a thick viscous solution which is then filtered and deaerated. Delusterants can be added at this point if desired. Dyes may also be incorporated with the acetate solution, but this method has not proved very satisfactory, and acetate rayon is usually dyed in the form of yarn or cloth.

(6) SPINNING

The viscous solution is forced through a spinneret in a downward direction into a shaft or cabinet in which there is a rising current of warm air. This evaporates the acetone quite quickly and leaves a filament of soft, semiplastic cellulose acetate. This is drawn out of the cabinet and wound on a bobbin or spool which turns at a faster rate than the filament being delivered from the spinneret. The result is that the filament is stretched, the molecules are oriented, and the strength is increased. It is possible to reel off more than 200 yd of acetate rayon per minute.

Note the important difference between acetate rayon and viscose or cuprammonium. Viscose and cuprammonium rayons are regenerated cellulose, but acetate rayon is an ester of cellulose, a real synthetic fiber.

This rayon is made in the two dimensional types, continuous filament and staple fiber. The continuous filament is made in regular (bright or dull), high impact, and saponified (a high-tenacity rayon). The regular has a normal tenacity of 1.25 to 1.5 gm/denier and an elongation of 20 to 25% at the break. The wet tenacity is about two-thirds of the dry. The size of individual filaments runs from 1.5 to 4.0 denier, and the yarns from 45 to 300 denier. The tensile strength of regular acetate rayon is about 23,000 psi.

Acetate rayon yarns are numbered by means of three figures, one giving the denier of the yarn, one the number of filaments, and one the number of twists per inch. For example, a 150/52/3 yarn would be a 150 denier yarn made with 52 filaments having three turns per inch.

HIGH-TENACITY ACETATE RAYON

Previous to World War II British Celanese, Ltd., had been developing a high-tenacity acetate rayon, and in 1941 the Celanese Corporation of America began to manufacture it under the trademark Fortisan. This material is made by the proper combination of stretching and saponification. The yarns are stretched at high temperature while still in the plastic state, and are then saponified. It is claimed that all the acetyl groups are removed during this saponification, leaving a substance that has the same structural unit as cellulose. If this is true, then Fortisan is not an acetate rayon, but a regenerated rayon in which the regeneration is accomplished in a different way from the method used in either cuprammonium or viscose rayons. It is assumed that in Fortisan the molecular chains are so highly oriented and bound together that the strength is higher than that of any textile fiber.

The tenacity of Fortisan is 7 gm/denier, and its tensile strength is 140,000 psi cross-section (stronger than iron wire). It has some outstanding properties which make it decidedly different from other rayons. Its loss in strength when wet is smaller than that of other rayons, being only 15 to 25%. Its regain of 9.8% is about halfway between that of viscose and regular acetate rayon. One very desirable physical property is that the elongation is not appreciably affected by moisture. Its elongation is 6 to 6.5%, either dry or wet. It is more resistant to heat than viscose, and it can be ironed safely at 20° C higher than viscose. The filaments can be made in small denier; 0.7 denier and a wide range of denier in yarns is possible.

One objection to high-tenacity acetate rayon is the stiffness which we would expect because of the high degree of orientation. A recent patent[7] assigned to du Pont claims to overcome this difficulty. According to this patent, high-tenacity yarn with an elongation of only 6% is passed at the rate of 15 ft per minute through an 18-in. tube heated to a little over 200° C. After such treatment the yarn is found to have elongations of 9 to 11%.

In 1943 Eastman was producing a high-impact-resistant quality of acetate rayon known as Koda. The tenacity of this rayon is not much different from the regular (1.3 to 1.6 gm/denier), but its elongation at the break is twice as much (45 to 50%). This means that it will absorb more work before it is broken, or in other words, it will resist sudden impacts, such as would rupture regular rayon or cotton, because of its extra high elongation. It was used for delivery parachutes during World War II.

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[7] Conaway, U.S. Patent 2,346,208 (1944).

PROPERTIES OF ACETATE RAYON

The physical properties of acetate rayon are controllable within rather wide limits by regulation of the spinning operation. The size and strength of the final filaments are controlled by the proper relation among the size of spinneret orifices, the rate at which the spinning solution is extruded, and the speed of the pick-up bobbins. Other spinning conditions such as temperature, humidity, and rate of air flow also affect such properties as elasticity and elongation.

Let us look at the good and bad properties of acetate rayon. Acetate rayon has a natural silklike suppleness, which gives to it outstanding draping qualities. It has sufficient resilience to make it fairly resistant to wrinkling and creasing, without the addition of crease-resistant resin finishes.

One property by which acetate rayon differs especially from other rayons is its low moisture absorption. The normal regain at 65% R.H. of viscose and cuprammonium is 11%; of silk, 11%; of cotton, 8%; and of wool, 15%; but acetate rayon regains only 6.5%. This low absorption of water is more important than it would seem. With a lower moisture content there is less swelling of the yarn or cloth, and that means that it will not become soiled as readily and that stains can be removed more easily, because they will not penetrate so much.

Acetate rayon has some bad properties, and yet certain ones can be adapted to give valuable effects. Recall that acetate rayon is an ester of cellulose and that one of the main properties of esters is that they can be saponified by hot alkalies. If this were done with acetate rayon, its properties would be altered completely. Therefore all scouring or dyeing operations must carefully avoid such a possibility. All acetate manufacturers refuse to assume any responsibility where fabrics have been subjected to any saponification, because such processes are so difficult to control.

Acetate rayon is soluble in acetone and some other liquids which are used for cleaning. In the early days this caused the dry cleaners a great deal of trouble, not so much with fabrics made entirely of acetate, for those could be handled in special ways, but with fabrics in which decorative effects were obtained by the use of acetate yarns. The National Association of Dyers and Cleaners, together with the Celanese Corporation, made a thorough investigation of the effect of a great many organic solvents, and mixtures of them, on acetate rayon. It is important that we know whether acetate yarns are insoluble, partially soluble, or soluble, or whether the liquid simply acts as a swelling agent.

Acetate rayon is insoluble in most alcohols except methyl and ethyl alcohols, in which it swells badly. It is insoluble in ethers, and esters above ethyl acetate. It is insoluble in carbon tetrachloride but is partially dissolved in chloroform. It is found that the solvent property of one liquid may be changed by the addition of another liquid.

The National Association of Dyers and Cleaners in 1940 issued a booklet called *The Cleaning, Dyeing and Finishing of Garments and Fabrics Containing Celanese Rayon Yarn.* The booklet gives data on whether or not certain common cleaning and spotting agents are safe for use on acetate rayon. This information is contained in Tables 38 and 39, which divide cleaning and spotting reagents into two groups, those which are safe and those which are not safe. It is understood that those considered safe are to be used at room temperature and without violent mechanical handling. The reagents are listed alphabetically.

The dry cleaning industry has adjusted its choice of solvents, so that today all fabrics are cleaned by methods that are safe for acetate rayon.

The solubility behavior of acetate rayon has been turned to good use in the manufacture of stiffened fabrics for collars, cuffs, shirt fronts, etc. By incorporating layers of acetate fabric between cotton or other fabrics and then moistening and pressing the cloth, a multi-ply cloth is obtained which is stiff and yet flexible and porous to moisture. The same effects may be obtained by weaving some acetate yarns in the cotton interlining and then treating with acetone.

The thermoplasticity of acetate rayon is one of its bad features. It is a well-known fact that, if acetate rayon is pressed with an iron that is a little too hot, the surface of the cloth will be unpleasantly glazed or even melted. This result is accompanied by a sticking of the iron. Housewives have learned to wash and iron acetate rayons as they would any fine fabrics, and so will press them with a warm iron. This thermoplastic property is valuable in the production of moiré patterns or embossed designs with heated engraved rollers. Such patterns on acetate rayon are permanent in spite of washing and cleaning, but such effects produced on natural fibers are very quickly destroyed by washing.

TABLE 38

SAFE SPOTTING AGENTS FOR ACETATE RAYON

- Acetic acid (not stronger than 28%)
- Ammonia
- Amyl acetate
- Benzene
- Butyl cellosolve
- Carbon tetrachloride
- Castor oil
- Chlorine bleaches (hypochlorites)
- D.C. solvent
- Formic acid (not stronger than 28%)
- Gasoline
- Glycerin
- Hexalin (cyclohexanol)
- Oxalic acid
- Potassium permanganate
- Soap (aqueous solutions)
- Sodium hydrosulfite (stripping agent)
- Toluene
- Trichloroethylene
- Turpentine
- Washing soda

TABLE 39

UNSAFE SPOTTING AGENTS FOR ACETATE RAYON

- Acetic acid (stronger than 28%)
- Acetone
- Amyl alcohol
- Chloroform
- Cresols
- Ether (diethyl)
- Ethyl alcohol
- Ethylene dichloride
- Formic acid (stronger than 28%)
- Lactic acid
- Methyl alcohol
- Tetrachloroethane

Staple Fiber Rayon

Staple fiber rayon is intentionally produced in short lengths (as compared with continuous-filament rayon) for blending with cotton or wool. In the early days of rayon production the object was to produce long continuous filaments like silk, which could be made into yarns as silk is, with a minimum of short waste fibers. This waste was sold to textile manufacturers, who took it because of its low cost and mixed it with other fibers (such as wool) in order to cheapen the product.

Later, rayon manufacturers became aware of the market for rayon intentionally made in short lengths so that it could be spun along with cotton, wool, or spun silk fibers, or spun into a yarn by itself (spun rayon). About 1930 the American Viscose Corporation put viscose staple fiber on the market, producing about 200,000 lb of it. By 1940 this had increased to 90,000,000 lb, and by 1949 the production of both viscose and acetate staple fiber was well over 250,000,000 lb. The rapid increase in consumption in this country is evidence of the need and usefulness of such a product.

Staple fiber is made in the same way as continuous-filament rayon up to the time of drawing off the coagulated fiber, except that spinnerets with many more openings are usually used. The filaments from several coagulating baths or cabinets (acetate) are combined to form a thick strand known as tow. This tow is then cut into the desired length. A wider range of denier is employed in staple rayon manufacture than for continuous filament. Rayon staple fiber is sold in seven different sizes: 1, 3, 5, 5.5, 8, 12, 16, and 20 denier.

In order to understand the reason for making such sizes we must keep in mind the purpose of making rayon staple fiber and the uses to which it is to be put. Some of it will be mixed with cotton, some with silk, some with wool to make woolens, and some with wool to make worsteds. If the mixed yarn is to be uniform, the rayon fibers must have approximately the same diameter as the natural fibers. The smallest denier would match silk, and the 3 denier would match cotton. The fineness of wool varies more than cotton, and so it is necessary to have a variety of staple fiber sizes to match it. For example, a 5.5 denier rayon is comparable with a wool which would be of about 62's quality (a fairly fine wool); the 8 denier rayon could be mixed with a medium fine wool, and the 12 denier with a coarse wool. The length of rayon staple fiber must also approximate the length of the natural fibers with which it is to be blended. Thus we have three classes of staple fibers based on length. Those to be mixed with cotton will be 0.75 to 2.0 in. long; those to be mixed with wool for woolens will be 2 to 4 in. long; and those to be mixed with wool for worsteds or mohair or with waste silk are 3 to 7 in. long.

Finishes for Rayon

Several special finishes may be applied to rayon, depending on the use to be made of the fabric. Three of the main objections to rayon are that it shrinks badly, particularly in the first washing; that it wrinkles and creases badly; and that, except for acetate rayon, it absorbs water too easily. Because of this last property, rayon goods are distorted and thrown out of shape by small tensions. Water absorption is also one of the fundamental causes of shrinkage. To overcome these difficulties rayon is given special finishes. Some finishes will improve the rayon in all these respects, but others are more specific in their effect.

Since rayon is so much like cotton we should expect, in general, that it could be finished by the same processes as cotton. This is true; the reader should refer to the water-repellent finishes (page 198) and shrinkproofing processes (pages 196–207).

Water-repellent properties can be conferred on rayon by most of the synthetic resin treatments or by the use of formaldehyde[8] with lactic acid and sodium chloride.

One of the leaders in the development of an anti-crease finish for rayon is Tootal-Broadhurst Lee Company (England). They give rayon the Tebilized finish, which consists of incorporating within the fiber water-soluble combinations of urea-formaldehyde condensation products of low molecular weight. The material is then cured at a high temperature in order to produce the insoluble resin. This treatment yields a fabric that is quite resistant to wrinkling and creasing; its dry strength is increased 30 to 50%, and its wet strength is almost doubled. It also shrinks much less.

The shrinkage of rayon can be decreased by most of the methods used for cotton, but there is one process which differs markedly from all of them. This is the Definized process of the Alrose Chemical Company. It is based on the premise that shrinkage is due to strains and stresses imposed upon yarns and fabrics during manufacture, resulting in a temporary set. If the fabric is dried in this strained condition, the individual yarns do not have their original dimensions, and when the cloth is washed they become relaxed, and swell and shrink in an effort to regain their original length. The Definized process consists of treating the material with a swelling agent. According to Shapiro,[9] "Under controlled swelling conditions the fibers become somewhat plastic, and the cellulose molecules or micelles are permitted to re-orient themselves within the fiber to a relaxed, strainless configuration. No chemical change occurs in the cellulose molecule, and the stabilization does not depend on the deposition of any foreign material in the fibers." According to this process, rayon is treated with a 40 to 50% solution of NaOH at about 100° F. It is then neutralized with acid (H_2SO_4), rinsed, and boiled under relaxed condition.

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[8] Brit. Patent 575,964 (1946).

QUESTIONS

1. What is the official definition of rayon according to the Federal Trade Commission? How does the British definition differ from this?
2. Name the three kinds of rayon. Name some of the large producers in this country, together with their brand names.
3. What general sequence of operations is used in the manufacture of these rayons? Which rayon is chemically different from the other two? Explain this difference.
4. In what two forms is rayon manufactured?
5. State the steps in the cuprammonium process.
6. Discuss the properties of viscose rayon—absorption of water, tenacity, elongation, etc.
7. How does the elongation of viscose rayon vary with the humidity? with the extent of orientation?
8. How is increased, or high-degree, orientation in rayon attained? How great a tenacity can be developed in this way?
9. Explain how rayon can creep in both directions.
10. Compare viscose rayon with cotton from the standpoints of (*a*) wet and dry strength, (*b*) action with mineral acids, (*c*) oxidizing agents, (*d*) strength, and (*e*) abrasion resistance.
11. State the steps in the commercial manufacture of viscose rayon.
12. What is accomplished by the stretching operation in rayon manufacture?
13. What valuable property of rayon must be partly sacrificed in order to get high tenacity?
14. Mention some of the important brand names for high-tenacity viscose rayon.
15. How can rayon be delustered? Why is this desirable?
16. How can a crimp be put into rayon yarn?
17. What are the best-known brands of acetate rayon?
18. What is the connection between acetyl content and the physical properties of the filament of acetate rayon?
19. Outline the steps in the commercial manufacture of acetate rayon.

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[9] *Rayon Textile Monthly*, December 1946.

20. How is Fortisan made? Who makes it? How does it differ chemically from Celanese?

21. What is meant by a high-impact-resistant rayon?

22. What are some of the desirable and undesirable properties of acetate rayon?

23. Name some organic solvents which will dissolve acetate rayon. Name some common solvents which will not dissolve acetate rayon and therefore may be used for spotting it.

24. What is staple fiber rayon? What length of staple rayon would be blended and spun with (*a*) cotton, (*b*) wool for worsteds, (*c*) wool for woolens?

25. How can rayon goods be made crease-resistant? water-repellent?

26. What is the Definized process?

9 · Wool

Wool is the oldest known and most important animal fiber, and, except in tropical countries, it is the fiber most used for outer wear. It has all the essential properties of a textile fiber (see page 105). Its length is good, its fineness superior; it is soft and elastic; its scaly surface gives it good spinning quality, and its strength is sufficient for the purposes for which it is used.

It will be understood that the word wool refers to the fiber which makes up the fleece of domestic sheep. There are other fibers similar to wool, such as mohair and cashmere, but they are the products of goats and are not considered real wool. Sheep which produce wool are bred and raised in almost every country in the world, but the major production of wool is confined to a few countries. Great Britain, Russia, the Argentine, British South Africa, and the United States are large producers, but Australia and New Zealand produce almost as much as all of these combined. These two sources make up about one-third of the world's supply. It appears that the position occupied by the British Empire in the world's wool market is about the same as that of the United States in the cotton market.

Most animals, especially in the wild state, produce two kinds of hair, (*a*) an outer growth of long, stiff, coarse hair, sometimes called beard hair or guard hair, and (*b*) an undergrowth of softer, finer, more elastic hairs. When such animals are domesticated, the long, straight, stiff hairs are gradually bred out, and the fine soft hairs increase in number. The domesticated sheep is a good example of this. However, if a few generations of sheep are neglected, the quality of the wool begins to show signs of retrogression.

The quality of wool for textile purposes depends mainly on two things, the breed of sheep and the location on the body. Wool may be classified as either long or short, depending on the breed of the animal. Merino and Rambouillet wools are short wools, and Lincoln and Leicester wools are long. Another and finer classification is based on quality. Quality of wool is a rather vague and indefinite term, but it refers to the size and type of yarn for which the wool is suitable. The fleece of a single sheep can be divided into as many as nine or ten different qualities. For example, the wool from the shoulders and sides is considered the best, whereas the wool from the legs is the poorest quality. Before wool is used, these various qualities in the fleece must be separated. This is known as wool sorting, and it requires an expert. Usually the breed of sheep determines whether the wool will be long or short, and the sorting divides it into qualities based on whether it is fine or coarse, stiff or soft.

PHYSICAL STRUCTURE OF WOOL FIBER

The wool fiber may be considered a shaft which grows from roots imbedded at the bottom of the hair follicle. This shaft consists of three structural parts, the epidermis, the cortex, and the medulla.

The *epidermis*, or cuticular layer, is the outer surface of the fiber, made up of flat, irregular horny scales arranged in a serrated pattern like fish scales or a shingle roof. This serrated appearance can be seen under the microscope, and wool fibers are easily identified by this appearance. The free ends or edges of these scales protrude or project outwards, pointing toward the root of the fiber. This scaly epidermis serves as a protection for the main part of the fiber, and also gives it some rigidity, which it would not otherwise have. The arrangement and type of scales on wool have a great deal to do with its suitability for different purposes.

The average width of these scales is about 0.036 mm, and their height is about 0.028 mm. The arrangement of scales in the epidermis is an overlapping one, the bottom part of each scale being concealed by the top of the one below it, and there is also a certain amount of sidewise overlapping. The amount of each scale that is visible (the visible length) is a characteristic which distinguishes wool from other hair fibers. For example, the visible scale height in fine wool is 0.008 to 0.010 mm, in coarse wools 0.014 to 0.018 mm, whereas in mohair it is about 0.020 mm.

The fineness of wool fiber has much to do with the number of scales that will be required to cover the shaft. In a fine wool one scale is enough to go all the way around the fiber, so that it looks like a series of funnels set inside each other, with the free edges projecting away from the shaft of the fiber. As the diameter of the fiber increases, the number of scales will also increase. The visible height of the scales also increases, which means less overlapping; this in turn means a smoother surface. The appearance of a coarse wool is therefore one of many scales lying up tight along the fiber. This makes a coarse wool smoother and more lustrous than a fine wool.

The *cortex* constitutes the main portion or body of the wool fiber. It consists of long, slightly flattened and twisted spindle-shaped cells. These cortical cells are about 0.080 to 0.110 mm long and 0.002 to 0.005 mm wide. The cortex of the fiber is mainly responsible for the strength and elasticity of wool, and its dyeing property.

The *medulla* is a narrow channel that runs lengthwise through the fiber and is loosely filled with medullary cells of various shapes. In fine wools it may be only a single chain of such cells, whereas in coarse wools several chains lie parallel. The size of the medulla varies greatly, and the volume of wool fibers occupied by the medulla may run from 10 to 80%. It is probably through the medulla that solutions of wet processing treatments and dyes penetrate the fiber.

The three structural features just discussed vary considerably among appendage fibers. The most important of such fibers are wool, mohair, cashmere, camel's hair, alpaca, llama, vicuña, and horsehair. These are arranged in an order dependent upon changes in the structural features, with wool at one end and hair at the other. These changes are shown in the accompanying table. This shows that there is a great difference among the appendage fibers. Because of such a difference, we should not speak of wool as a hair. Hair is one thing and wool is another. The many uses to which wool is put are based on its special properties, which are different from those of hair.

	Wool	Hair
Scales	Projecting with pointed edges	Lie closer with rounded edges
Medulla	Indistinct	Well marked
	Wavy	Straight
	Felting property	No felting

Now let us look at the connection between the structural units of wool and its special properties. We shall discuss the relation between scales and felting and luster; the relation between the cortex and waviness and setting; and the relation between the medulla and dyeing.

Before proceeding, we must understand what is meant by felting. The first thought is that it is an operation or a property which results in the formation of a felt. This is true, but the making of a felt is an extreme case. Various lesser degrees of felting may be used to obtain special effects. In the finishing of practically all woolens, an operation known as fulling or milling is used. In principle, this consists of rubbing and pounding woolen cloth while it is soaked with slightly alkaline soap solution at high temperature. The result is a snappy, compact, firm, opaque surface in which individual fibers are consolidated and packed tightly around and among each other. During fulling, the cloth always shrinks. Incidentally, the milling operation can be used to incorporate very short staple wool shoddy into heavy woolens such as overcoats.

What is the connection between the scales on wool and its felting property? Originally it was thought that there was a very important connection, because other fibers (silk, cotton, linen, etc.) that have no scaly epidermis cannot be felted at all. It was thought that felting was caused by the interlocking of the scales of adjacent fibers, and that this was assisted by mechanical manipulation, the result being a contraction or shrinkage and a compacting of the fibers. However, it was found that some wools would not felt well, even though a microscopic examination showed that they had plenty of projecting scales. That is, the degree of scaliness is not a measure of felting property. Hence, the scale characteristic of wool is not the main cause of felting property. On the other hand, when the free edges of scales are removed by a chlorination treatment (page 278), the wool is rendered fairly nonshrinkable. A more detailed discussion of felting will be found on page 256.

The connection between scales and luster is more obvious. Luster is the reflection of light from a surface and the smoother the surface, the more lustrous it will be. Therefore those wools in which the scales lie up close to the shaft of the fiber, with fewer projecting edges, will be the more lustrous. This is true of the long, coarse wools like Lincoln and Leicester. The difference in luster between woolens and worsteds should be pointed out. Worsted yarn is composed of more parallelized fibers, and a cloth woven from such yarns would be smoother than one made from woolen yarns with their scribbled arrangement of fibers. The preservation of the luster of a cloth depends solely on the preservation of the surface. This means the avoidance of all severe chemical treatments, all high temperatures, especially when the wool is dry, and any mechanical tearing or breaking of surface fibers.

The cortical cells make up the true fibrous part of wool and are responsible for its strength and elasticity. In fine wools the cortex is not uniformly developed, so that on one side of the fiber there will be a contraction causing a bend in the shaft of the fiber. Because of this unevenness in the cortical cells, wool has its characteristic waviness which is an important factor in its spinning quality. The number of waves per inch varies with the diameter of the wool. In fine wools there are 24 to 30 waves per inch, in medium wools 11 to 16, and in a coarse wool like Leicester, 3 to 5 waves per inch. When wool is stretched, the cortex must accommodate itself to distortion. If wool is heated while wet, it softens somewhat and may be distorted and shaped. The cortex adjusts itself to this new form, and if the wool is held in the same form until it cools and dries, we say that it has been set. The wool will often retain this new form for long periods of time. As certain chemical treatments assist in the setting of wool, we shall reserve a fuller discussion of this subject until we have studied the chemical properties of wool (page 267).

The medūlla is the central canal or channel of the wool fiber. Even though it is partially filled with cells, there are channels between the cells through which liquids can pass. When wool is dyed, the solution of dyestuff enters the fiber through the medulla. The scales are impervious, so that the solution of dye cannot get into the fiber through the scales. The only possible entrance along the side of the fiber is at the joints of the scales. When a fiber is dyed, the solution passes into the medulla and shows through the scales. This makes the longitudinal view of dyed wool different from a cross-section view. It is well known that the color of a cut pile fabric is deeper and richer than that of a woven cloth.

If sheep are poorly fed and cared for, they may produce a wool known as kempy wool, or kemps. Such fibers have tight rounded scales and an imperfectly developed medulla. Their felting property is very poor, and it is difficult to dye them. Kempy fibers usually show up as white specks on a dyed cloth.

The skin of animals on which hair grows is provided with numerous small depressions called follicles, at the bottom of which are found the roots of the hairs. As the hair grows, it passes up the length of the follicle and out above the surface of the skin. There are two kinds of glands just below the surface of the skin. The sudorific or sweat glands, which excrete perspiration, feed into the surface of the skin, so that wool or hair will pick up varying amounts of perspiration salts. Then there are fat or oil glands, which excrete oil into the hair follicle. This greasy material covers the hair, or fiber in the case of wool, and serves as a protection against mechanical damage to the fiber. It is well known that some people perspire freely and others do not, and that some people have a greasy or oily skin and others do not. These individual variations also occur with sheep but seem to depend upon the breed. The wool of some breeds is always very greasy, but with other breeds the amount of grease is small. As a rule, the fine wools have a great deal of grease and the coarse wools have much smaller amounts. We shall therefore expect raw wool, as sheared from the sheep, to be contaminated with perspiration salts and grease, but we shall be surprised at the amount of these so-called impurities. The composition, or analysis, of raw wool will vary greatly because of many factors, but we can approximate average compositions, two of which are shown here. It is understood that these are only averages, but they illustrate the difference between fine and coarse wools.

Composition of Raw Wool	Percentage in Fine Wool (Merino)	Percentage in Coarse Wool (Lincoln)
Moisture	16.8	17.1
Grease	20.2	6.7
Suint	9.3	2.3
Sand and dirt	7.2	5.1
Clean fiber	46.5	68.8

Note how raw wool decreases in weight when it is washed. A typical long coarse wool will lose one-third of its weight, and a fine wool will lose more than one-half its weight. The coarse wool may be called a low-shrinkage wool and the fine wool a high-shrinkage wool. The use of the word shrinkage in this way has nothing to do with any dimensional change.

Suint is the name applied to dried perspiration which accumulates on wool and which is soluble in warm water. It consists of a mixture of potassium salts of organic acids (mostly oleic, palmitic, and acetic), together with a small amount of sulfate and phosphate. If raw wool is washed with warm water and the wash water is evaporated to dryness, a white solid will be left. If this white solid is ignited it will char and become very black, and after this carbon has burned off, a white solid is left which is principally potassium carbonate.

Wool grease is an impurity in raw wool, but if it is recovered from the scouring baths in which wool is washed it has a good market value. Wool grease is insoluble in water but can be partially emulsified by it, and it is easily emulsified with warm soap solution. It is soluble in organic solvents. When first separated from waste scouring baths, it has a dirty yellow color and a sheepy odor, but after purification it is a very pale yellow with no odor. Its melting point varies from 38 to 44° C. The purified grease is known as lanolin. Wool grease is an ester of high-molecular-weight fatty acids, but it is not a true fat because it is not a glyceryl ester. The exact composition of wool grease has not been determined, but Drummond and Baker[1] found that it consists of a saponifiable part and an unsaponifiable portion. The unsaponifiable part is made up mostly of cholesterol, a high-molecular-weight alcohol, $C_{27}H_{45}OH$. The saponifiable portion contains esters of high acids such as cerotic, stearic, and palmitic acids, together with small amounts of free fatty acids.

THE SCOURING OF RAW WOOL

The washing of raw wool involves the removal of three types of substances, wool grease, suint, and extraneous dirt. Wool grease is insoluble in water, soluble in organic solvents, and very easily emulsified with soap solution; it is more easily emulsified than any of the other common fatty materials. Thus the grease could be removed from raw wool either by the use of organic solvents or by ordinary soap washing. Suint is soluble in warm water and so offers no special problem. The third substance to be removed consists of extraneous dirt which has been picked up by the sheep during its life. Much of this is heavy dirt like sand.

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[1] *J. Soc. Chem. Ind.*, **48**, T232 (1929).

Experiments have been made with solvent extraction methods in which wool is immersed in a solvent such as light naphtha or carbon tetrachloride. The solvent dissolves the grease but none of the other impurities. It must then be dried and washed with soap solution to remove suint and dirt. This method has not proved very successful. There is too great a loss in solvent when it is recovered by distillation, and some spinners claim that too much grease is removed.

The method almost universally used is scouring with warm soap solution. This is done in three or four "bowls" (long tanks) containing soap and soda ash. The amount of soap in the first bowl varies from 0.3 to 1% of the weight of the wool, depending on the greasiness of the wool; the soda ash equals 1 to 2% of the weight. The temperature runs from 40 to 60° C, the lower temperature being used for fine wools. No caustic should be used, and the soap should be carefully selected. This is a low-temperature washing, and therefore an easily soluble soap should be used. Formerly potash soaps were preferred, but it has been shown that sodium soaps made from oleic acid are equal to or better than potash soaps. One of the most important factors is the method of agitation. The conditions in the scouring bath are such that felting of the wool may very possibly occur; the bath is warm, it is slightly alkaline, soap is present, and there must be some agitation. If the wool is handled too roughly, there will be a great deal of felting, and later on, when the wool is carded or combed, many fibers in the entangled mass will be broken. Of course this results in waste short fibers. There is a market for these waste fibers, but it is a lower-priced market, and so every effort is made to prevent felting during scouring. The ease with which wool grease is emulsified with soap is a great advantage, because if it were necessary to tumble the wool as much as is done in cotton laundering it would be hopelessly tangled and felted.

The usual procedure is to start the wool in the first bowl, as indicated above, and then pass it to the second and then the third bowl. The concentration of soap and soda is decreased in successive bowls, so that the last one does more rinsing than washing.

The scouring baths may be saved and the grease recovered from them.

It would be desirable to have some way to scour wool more quickly and yet maintain a minimum of felting and damage. This would require a higher temperature and higher alkalinity. Experiments have been made along this line, and it appears that some sort of treatment with formaldehyde or aldehyde-bisulfite addition compounds offers some possibilities for protecting the wool. Dubeau and Vincent[2] point out that sodium bicarbonate is formed when wool is scoured with soap and soda ash (Na_2CO_3), and that the rate of scouring is maximum when the ratio between carbonate and bicarbonate is 1 : 1. Therefore it is claimed that, if sodium bicarbonate is added to the first bowl and the ratio of 1 : 1 is maintained, the time for scouring will be decreased 50% and the scoured wool will be cleaner, more uniform, and easier to card.

We shall find that wool is very sensitive to alkalies. This may be due to the ease of hydrolysis of proteins by alkali, or to the reaction of free carboxyl groups with the alkali. Wool contains some free COOH groups, and more of them are formed during any protein hydrolysis that may take place. Recall that soap is a salt of a strong base and a very weak acid, and therefore in solution it will be hydrolyzed to form the weak acid and the strong base

$$RCOONa + HOH \rightleftarrows RCOOH + NaOH$$

Wool absorbs the alkaline portion selectively, leaving the free fatty acid, some of which may attach itself to the fibers. This fatty acid should be destroyed by the alkalinity of the scouring baths, but there is always the chance that clean wool may come out with small amounts of fatty acid. The objection to this is that the wool will develop a bad odor after it is stored. A final rinse with dilute soda ash solution should prevent this.

PHYSICAL PROPERTIES OF WOOL

It is well known that wool is a highly prized fiber for textiles in spite of its cost. Many desirable features about woolen and worsted cloths and knit goods cannot be excelled or even duplicated by other textile fibers, and wool dominates the special fields in which it is used. The superiority of wool depends entirely on its physical properties, as no chemical treatment is given wool during its conversion from clean scoured wool fibers to the finished product. This statement will be modified when we discuss some of the newer methods for processing wool in order to improve it. Even though wool is not given chemical processing during its manufacture, its chemical properties must be clearly understood when dealing with the care and maintenance of wool goods. These properties will be discussed later. At this point we are interested in the physical properties of wool, upon which its quality and uses depend.

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[2] *Am. Dyestuff Reptr.*, **35**, 469 (1946).

In a general way these properties can be divided into the two extremes, good and bad. Among the desirable properties of wool are its fineness, softness, resilience, and elasticity; it can be stretched and still recover its original shape; it is the warmest fiber; it can be set and made to retain a new shape or dimension for a long time; it can be felted and compacted into materials for special purposes. Among the undesirable properties of wool are its low strength (it is one of the weakest of the textile fibers); its felting property (when felting is not desired); and its tendency to shrink. The magnitude of all these properties of wool varies over a wider range than most textile fibers because of the variation in breeds of sheep, climate, feeding, etc.

As we discuss the physical properties of wool, which are so important in the determination of its suitability for textile uses, we must keep in mind the structural units of the wool fiber, the epidermis, the cortical cells, and the medulla.

THE DIMENSIONAL CHARACTERISTICS OF WOOL

The *length* and fineness of wool fibers vary greatly, depending on the breed of sheep. Table 40 shows the length of various wools, which are divided into fine, medium, and coarse wools.

TABLE 40

LENGTH OF WOOL FIBERS

Fine		Medium		Coarse	
Breed	Length, in.	Breed	Length, in.	Breed	Length, in.
American Merino	1.5–3.0	Corriedale	3.0–7.0	Romney	5–6
Rambouillet	2.5–3.5	Cheviot	3.0–6.0	Leicester	6–8
Australian Merino	3.0–5.0	Oxford	3.0–5.0	Cotswold	10–14
		Shropshire	2.5–3.5	Lincoln	8–12

Clothing or carding wools, which are used in the manufacture of woolens, have a maximum length of about 3 in., and combing wools vary from 2.5 to 7 in. in length.

When wool is combed, the long and short fibers are separated; the long ones are called tops, and the short ones noils. Tops are used for spinning worsted yarns, and noils for woolen yarns that go into woolen fabrics, shawls, and goods that are to be heavily felted.

The *fineness* of wool fibers varies considerably even within one quality or grade of wool. Table 41 shows the fineness range allowable under the official standards set up by the U.S. Department of Agriculture. The table gives the minimum and maximum average diameter in microns for different grades of wool. A grade of 60's means that such wool is suitable for spinning a wool yarn of size 60.

TABLE 41

FINENESS OF GRADES OF WOOL

Grade	Average Diameter, microns	
	Minimum	Maximum
80's	18.1	19.5
70's	19.6	21.0
64's	21.1	22.5
60's	24.1	25.5
58's	25.6	27.0
56's	27.1	29.0
50's	29.1	31.5

The *strength* of single wool fibers is poor compared with other textile fibers. One reason for this is the lack of orientation in the fine structure of wool. In spite of the lack of homogeneity and the high molecular weight of fibrous materials, they are not completely amorphous but show definite crystalline portions (highly oriented portions). In these portions of the fibers there are compact bundles of long-chain molecules in parallel arrangement. In general, the strength of fibers is proportional to the degree of orientation, so that wool, with its low orientation, should be weak. Flax, ramie, and nylon are the highly oriented fibers, and thus the strongest; silk and cotton show medium degrees of orientation and therefore are weaker; rayon can be made with low, medium, high, or very high orientation and thus has a wide range of possible tensile strengths. All the hair fibers are of low orientation, but wool ranks well among them.

Table 42 shows the relations among fineness, single fiber strength, and tensile strength. These data are the result of work done in the laboratories of the Forstmann Woolen Company and are reported in Matthews and Mauersberger's *Textile Fibers*, John Wiley & Sons, 5th Edition, 1947, pages 538–540. All the figures in Table 42 are averages of a large number of tests and are subject to wide variations for each type of animal fiber. Note that a strong individual fiber does not necessarily mean a high tensile strength. The fibers are arranged alphabetically.

TABLE 42

FINENESS AND STRENGTH OF ANIMAL FIBERS

(65% R.H. at 72° F)

Fiber	Average Fineness, microns	Strength	
		Single Fiber Breaking Strength, gm	Tensile Strength, psi
Alpaca	27.0	10.43	25,800
Camel's hair, fine	20.7	5.6	25,400
Camel's hair, coarse	26.6	10.38	25,700
Cashmere	15.0	2.54	20,500
Cow hair	187.0	603.33	28,700
Horsehair, tail	181.0	488.57	27,100
Horsehair, mane	129.0	230.00	25,500
Human hair, fine	58.6	66.36	34,600
Human hair, coarse	84.8	133.75	33,800
Wool, fine	19–23	4.8–7.1	22,700–23,400
Wool, medium	27–33	10.3–16.0	25,800–26,600
Wool, coarse	36–38	20.3–23.6	27,400–29,100

The *elasticity* and *elongation* of wool are perhaps its most important physical properties. Ease of stretching can be measured by determining how much weight is required to stretch a fiber a given amount (say 1%) at a fixed humidity and temperature. Wool is more than twice as stretchable as viscose rayon, and about 50% more stretchable than cotton. The ability of wool to recover its original length after stretching is very high compared with other fibers, being exceeded only by nylon. Under certain controlled test conditions wool will recover 89%, silk 70%, viscose 52%, and cotton 45%. The elongation of wool exceeds that of any other textile fiber. It will stretch an average of 30% before it breaks, whereas silk will stretch only 13%, nylon 20%, and standard viscose only 18%.

We shall discuss further the elastic property of wool after we study the chemical structure of wool and understand the types of cross-linkages found in wool fiber.

The *waviness* (crimp) of wool is a factor which contributes to spinning quality. The number of crimps or waves per inch depends on the breed of sheep, the fineness of staple, and other variables. The relation between fineness and waviness is so general that many wool sorters base their judgment of fineness on the amount of crimp. However, this has been shown to be subject to much error. In general, the very fine wools will have 22 to 30 waves per inch, fine wools 14 to 22, medium wools 8 to 14, and coarse wools up to 8 waves per inch.

The *hygroscopic property* of wool must be discussed at some length. Wool is more hygroscopic than any of the vegetable fibers and is also somewhat more so than silk. It may absorb as much as 25% moisture and yet feel dry. The amount of water absorbed depends on the temperature and humidity conditions under which wool is stored. Under average conditions wool will absorb from 10 to 15% moisture. The literature of textile technology is somewhat confusing when it deals with the moisture relations in wool. In order to clarify this matter, we must understand the exact meaning of the terminology employed.

There are two kinds of water in wool. The first is hygroscopic water, which is water mechanically held in the pores of any hygroscopic material. This kind of water can be evaporated by means of heat and then regained when the material is exposed to a moist atmosphere. In other words, it is ordinary moisture. The other kind of water is water of hydration, which is chemically bound to the wool substance. If wool is heated to such an extent that this water is driven off, the wool becomes weak and brittle, and it does not regain its original properties when exposed to moist air. It is evident that the wool has been chemically altered through a loss of water of hydration. This idea is supported by the general agreement that it is safer and better to let wool dry in the air instead of using artificial heat, which usually involves some local overheating.

In all discussions of the *moisture relations* in wool, it is the hygroscopic water that is involved, because it is this water that can be lost and gained without changing the chemical structure of the wool. There are two ways in which the amount of moisture in wool can be expressed. When we say that wool has a certain percentage of moisture, we base the percentage on the air-dry weight of wool. For example, if 10 gm of air-dry wool loses 1 gm when it is heated to a bone-dry condition, the moisture (the 1-gm loss) is 10% of the air-dry weight. We therefore say that this wool, at the particular humidity and temperature at which it was weighed, contains 10% moisture. If it were conditioned at some other relative humidity, the per cent moisture would not be 10%.

TABLE 43

MOISTURE REGAIN OF WOOL IN THE GREASE

Relative Humidity, %	Regain (on Dry Weight), %
30	6.0–8.5
40	7.2–9.7
50	8.5–11.0
60	9.6–12.2
70	11.0–13.0
100	39.0–48.0

When we speak of per cent moisture regain, we are basing it on a bone-dry weight of wool. For example, if a 10-gm sample of perfectly dry wool is exposed to moist air it may absorb 1.5 gm of moisture, which is 15% of 10, and so we say its regain is 15%. The amount of regain will vary with the relative humidity of the atmosphere to which the wool is exposed. This is shown in Table 43.

Three kinds of weights are used in textile analysis and testing. The air-dry weight is the weight of a mass of fibers after it has established an equilibrium in any particular humidity and temperature. If the fibers are dried in an oven until all the moisture is driven off, the weight is called the bone-dry (or oven-dry) weight. Then there is the condition weight. The word condition in the textile industry refers specifically to moisture condition. If wool is too dry for good spinning we speak of conditioning it, that is, exposing it to more humid atmosphere until it has attained the proper condition. Thus the word condition is used as a verb to describe the attainment of a state of proper moisture content. The conditioned weight of a sample or batch of wool is the weight that the wool would normally have in a normal atmosphere. This weight may be considered as the bone-dry weight plus an amount of moisture that it has regained in order to reach the conditioned weight. The amount of this regain is expressed in terms of percentage, the percentage of regain, or the regain. Thus regain is a percentage of weight to be added to bone-dry weight to equal conditioned weight. This is such an important factor that various official agencies and testing organizations have established standard regains for all commercial fibers.

Standard regains established by the American Society for Testing Materials are for 70° F and 65% R.H.

Raw cotton	7.0
Cotton yarn	7.5
Mercerized cotton	8.5
Cotton cloth	6.5
Scoured wool	13.6
Worsted yarn (Bradford)	13.0
Worsted yarn (French)	15.0
Silk	11.0
Rayon (regenerated)	11.0
Rayon (acetate)	6.5
Wool tops	15.0
Woolen yarn	13.0

Because of variations in weight with atmospheric conditions, wool is often bought and sold on a standard regain basis. Suppose that we have received 1000 lb of wool and are to pay for it on a 15% regain basis. We do not necessarily pay for 1000 lb, but we pay for the conditioned weight of the wool, which is 115% of its bone-dry weight. So we determine the per cent moisture in the wool and find, for example, that it is 8%. That is, there are 80 lb of moisture in the 1000 lb, leaving 920 lb of bone-dry wool. The conditioned weight is 115% of 920, or 1068 lb, which is the weight we pay for at some agreed price.

The moisture content of wool has two important effects. Increased moisture decreases the strength and lowers the count of yarns. For example, a certain worsted yarn had a strength of 234 gm at 45% R.H., and only 191 gm at 85% R.H., a decrease of about 18% in strength. The effect of moisture on the count of yarn is shown below, using worsted singles:

Count at 45% R.H. =	39.09
65	38.08
85	36.03

This does not seem to be a very great difference, but if we calculate the difference in yards per pound it will seem much more significant. The difference between

45% and 65% is	566 yd per lb
65% and 85% is	1148 yd per lb
45% and 85% is	1714 yd per lb

The *effect of heat* on wool is not noticed much under 130° C unless the wool is exposed for a long time. When heated in dry air it begins to feel harsh and brittle at 115° C. It begins to scorch at about 200° C.

THE FELTING OF WOOL

We have already learned that felting is an inherent property of wool, as a result of which wool fabrics can be compacted or even converted into wool felt. The process of felting a woolen cloth to give it some desired finish is called milling or fulling, and it is done by rubbing and pounding the cloth with rocker-shaped wooden pieces called fulling blocks. During this time the cloth is wetted with hot soap solution, and the process is continued until the desired degree of felting has been reached. During the milling of a woolen cloth, considerable shrinkage takes place, and this shrinkage is acknowledged as being incident to the operation. But after wool cloth is in the hands of the consumer any shrinkage due to felting is highly undesirable, and hence various methods for shrinkproofing wool have been developed. These procedures will be discussed later. At this point we shall summarize the theories of the causes of wool felting and the work done on the development of some of these theories, especially the reports of Speakman[3] (England), Harris[4] (United States), and Freney[5] (Australia), all of whom have been prominent in this branch of wool technology.

The amount of felting in a wool cloth can be determined by the measurement of shrinkage either after hand washing or after some standard laundering operation. The second method is better because the laundering operation can be more standardized and the results are more reproducible.

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[3] *J. Textile Inst.*, **32**, T96 (1941).

[4] *Am. Dyestuff Reptr.*, **34**, 72 (1945).

[5] Society of Dyers and Colourists, *Fibrous Protein Symposium*, 176–192, May 1946.

It is now accepted that no one factor is the sole cause of wool felting, but that it is due to a combination of factors, each one contributing its undetermined share to the total effect. We shall discuss some of the theories proposed to explain the cause of felting, and then discuss some of the factors which are not causes but have to do with the extent, rate, or ease of felting.

There are five prominent theories to explain the cause of wool felting. It must be understood that none of these theories offers a complete explanation, but perhaps each one contributes something.

The oldest theory, and the one most accepted in the older literature, is based on the interlocking of the epidermal scales on wool fibers. The free edges of the scales become entangled, and during the milling operation there is a drawing together of fibers because they become hooked to each other. This theory is supported by two facts: that felting is more apparent under either slightly acid or alkaline conditions, and that under these conditions the amount of scaliness is increased. Therefore the scaliness of wool must be taken into consideration. This is perfectly logical, but it does not explain why some coarse wools with a good scaly epidermis do not felt well.

The migration of individual fibers has been proposed to explain felting. It is known that, under external stresses, such as milling, wool fibers will travel or creep toward their root ends, pulling adjacent fibers with them and increasing entanglement. This probably is important but cannot explain all the facts connected with wool felting.

Another theory emphasizes that fibers must be easily stretched and deformed, and must be able to recover after stretching. It is known that elongation is increased in acid medium and that deformation is increased in alkaline medium; the power of recovery is unaffected by dilute acids but is greatly reduced in alkaline media with a *p*H greater than 10. It has been shown that the ease of stretching is greatest at the same *p*H values at which felting is easiest. Thus there may be some connection between felting and the extensibility of wool.

Another theory has to do with the twisting of fibers when they have been placed in water or a saturated atmosphere and are free to move. Under these conditions the fibers will twist or revolve at a fair speed and finally come to rest. When transferred to a dry atmosphere, they will revolve in the opposite direction the same number of turns. This twisting ability of fibers may well play a part in felting, where fibers are wetted and subjected to alternating stresses.

The last theory is dependent on the tendency of wool fibers to curl under felting conditions, and it is based on inference rather than fundamental facts. The difference in the contractile properties of cuticle and cortex determines the curling tendency. When a wool fiber is placed in warm water the cortex tends to contract, but the cuticle has less contractile property, and therefore a curling or bending takes place. We know that when wool is felted it is swollen and is alternately stretched and released. Thus the contractile property of wool must play an important part. We shall learn that some of the oldest and best methods for shrinkproofing wool are procedures which attack the cuticle of the fibers. This reduces the effect of difference between the contraction of cuticle and cortex, and therefore reduces the curling tendency. The point is that, if treatments which reduce felting also reduce curling, then perhaps curling has something to do with felting.

Now let us consider some noncausative factors concerned in wool felting. One such is the arrangement of fibers in relation to each other and to the root ends and tip ends. Usually this is a quite random arrangement. However, experiments have shown that, if a cloth is made in which all the tip ends of fibers point in the same direction, a standard milling produces 25% less shrinkage than usual. This seems to be evidence that the arrangement of fibers has something to do with the amount of felting. Felting depends on the *p*H of felting solutions; more felting takes place at either high or low *p*H, but much less occurs at intermediate *p*H (neutral). However, *p*H above 10 is not good because it affects the chemical structure of wool. The part played by the cross-linkages in wool will be mentioned when we discuss the various methods for shrinkproofing wool.

THE CHEMICAL COMPOSITION OF WOOL

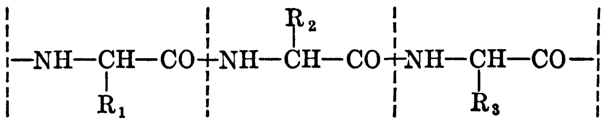
Wool is composed of five elements, carbon, hydrogen, oxygen, nitrogen, and sulfur. As most of the stability and instability of wool depends upon functional nitrogen and sulfur groups, we are chiefly interested in the proportion of these two elements in wool.

The N and S content of wool varies considerably. The percentage of nitrogen varies from 16.5 in Peruvian merino to 17.1 in Montevideo, the average of nine leading types being 16.84. The percentage of sulfur in wool varies from 3.1 in Lincoln to 4.0 in Cape merino. The average is 3.54. The difference between high and low sulfur wools seems slight, but if it is considered from a percentage difference, it is sizable; e.g., Cape merino has about one-third more sulfur than Lincoln.

When we studied cellulose in Chapter 6, we discussed its structure first and then explained its chemical properties on the basis of the structure. We shall do the same thing with wool. However, it must be clearly understood that the structures of these complex substances have been elucidated by the results of studies of chemical and physical properties. The properties come first, and then the structures. In outlining our present method of study we are taking advantage of an enormous amount of work which was done before any reasonable structure for wool could be proposed.

THE CHEMICAL STRUCTURE OF WOOL

Until 1925, as a result of the work of a great number of chemists, chief of whom was Emil Fischer, the protein molecule was supposed to be of a polypeptide nature, composed of 15 to 20 amino acids condensed with each other from the NH_2 group of one to the COOH group of another. This condensation would join molecules together by a peptide linkage. All these amino acids can be obtained from proteins by alkaline hydrolysis, and as all of them are found to be α-amino acids the following general formula was assigned to the protein molecule:



$$\vdots\text{—NH—}\underset{R_1}{\underset{|}{\text{CH}}}\text{—CO}\vdots\text{—NH—}\overset{R_2}{\overset{|}{\text{CH}}}\text{—CO}\vdots\text{—NH—}\underset{R_3}{\underset{|}{\text{CH}}}\text{—CO—}\vdots$$

This shows the condensation of three molecules of amino acids (enclosed between the dotted lines) which differ from each other in the size and structure of the radical R. We can therefore think of the protein molecule as a long polypeptide chain with fifteen to twenty different side chains. It is thought that about 50% of the weight of wool is due to these side chains.

This was about as far as the chemists could go, but in 1925 the physicists became interested in the long-chain compounds found in various fibers. Astbury[6] in England and Meyer and Mark[7] in Germany applied X-ray analysis to the study of various fibers.

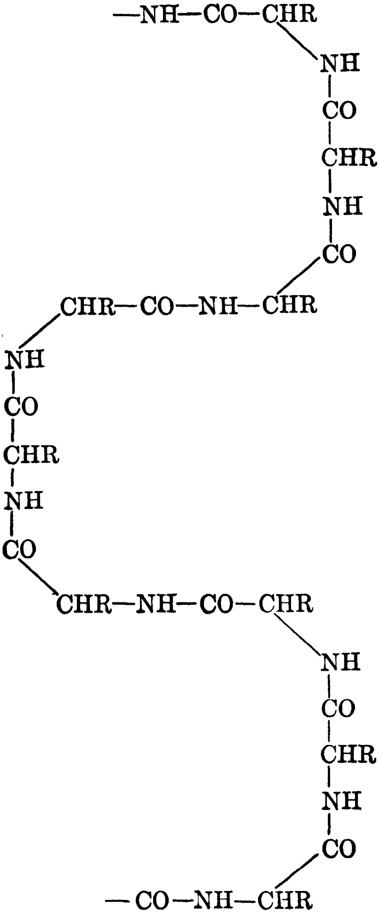


Figure 1.

They discovered that part of the protein fiber molecules orient themselves in a crystalline form; they measured distances and the length of repeated units in the pattern; they analyzed stretched fibers and found that the pattern of the stretched fiber was different from that of the unstretched and that in wool the original pattern was re-established after the wool recovered its original length. As a result of much work, Astbury and Woods[8] proposed the first working model for the structure of wool. Their structure showed the polypeptide chains of wool in a folded form which would unfold when stretched and then, owing to contractile forces, assume its original folded form when stretching tension was released. The particular type of fold (involving a hexagonal structure) was later shown to be wrong, and Astbury and Bell[9] proposed a model which seems to answer most of the questions connected with the physical and chemical properties. This structure is shown in Figure 1.

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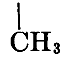
[6] *Nature*, **126**, 913 (1930).

[7] *Ber.* **61**, 1932 (1928).

In the Astbury and Bell structure of wool, the R's are considered as side chains. They are the carbon chain part of amino acids, and as there are fifteen amino acids in wool there must be fifteen different kinds of R's. This structure shows only a small part of one chain, but we know that there are many such chains lying parallel along the wool fiber, and our first concern would be with what holds these chains together. Outstanding workers in this field have been Speakman of Leeds University, England, and Harris, working at the Bureau of Standards, the Textile Foundation, and more recently at the Milton Harris Research Laboratories in Washington. In 1941 Speakman presented the Mather Lecture before the Textile Institute in England, on "The Chemistry of Wool and Related Fibers." The paper was published[10] and is such a well-organized and brilliant survey of the subject that much of the following material has been abstracted from it.

There are two main structural features in the wool fiber, the peptide chains (which have been shown previously) and the cross-linkages, of which there are two types, the salt linkage and the cystine linkage. Let us get a more extended picture of the peptide chain showing the side chains. First we shall assume the condensation of three molecules of alanine,



$$H_2N\text{—}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{—}COOH$$

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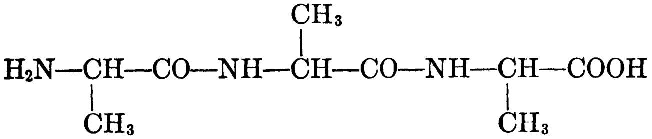
[8] *Trans. Roy. Soc.* (*London*), **A232**, 333 (1933).

[9] *Nature*, **147**, 696 (1941).

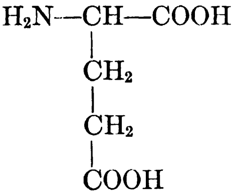
[10] *J. Textile Inst.*, **32**, T83–108 (1941).

the NH_2 group of one molecule joining to the COOH group of another molecule, with the elimination of HOH.



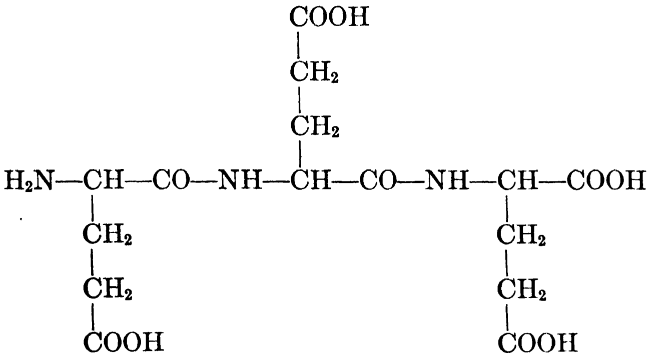
$$H_2N{-}\underset{\begin{array}{c}|\\CH_3\end{array}}{CH}{-}CO{-}NH{-}\overset{\begin{array}{c}CH_3\\|\end{array}}{CH}{-}CO{-}NH{-}\underset{\begin{array}{c}|\\CH_3\end{array}}{CH}{-}COOH$$

This compound has NH_2 and COOH groups, so that it could condense with more alanine to form a long chain in which the side chains (R's) are simple methyl groups. However, the side chains may be longer and more complex. We can illustrate this by condensing three molecules of glutamic acid,



$$H_2N{-}\underset{\begin{array}{c}|\\CH_2\\|\\CH_2\\|\\COOH\end{array}}{CH}{-}COOH$$

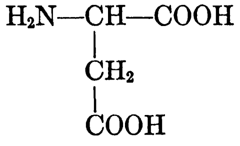
a dicarboxylic acid making up 15.3% of wool protein. This would give the structure



$$H_2N{-}\underset{\begin{array}{c}|\\CH_2\\|\\CH_2\\|\\COOH\end{array}}{CH}{-}CO{-}NH{-}\overset{\begin{array}{c}COOH\\|\\CH_2\\|\\CH_2\\|\end{array}}{CH}{-}CO{-}NH{-}\underset{\begin{array}{c}|\\CH_2\\|\\CH_2\\|\\COOH\end{array}}{CH}{-}COOH$$

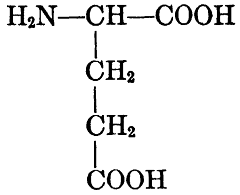
Note that the side chains have COOH groups which might condense with NH_2 groups from other amino acids, or they might form salts with NH_2 groups. The complexity of structure becomes apparent when we realize how many amino acids are combined in wool, and especially when we find some of them with two COOH groups and others with two NH_2 groups.

Wool has two amino acids with two COOH groups. They are



$$\begin{array}{rl} H_2N- & CH-COOH \\ & | \\ & CH_2 \\ & | \\ & COOH \end{array}$$

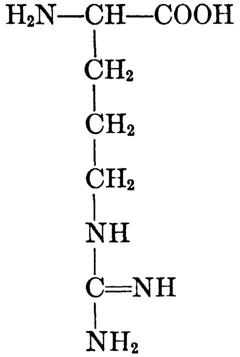
(aspartic acid 7.3%)



$$\begin{array}{rl} H_2N- & CH-COOH \\ & | \\ & CH_2 \\ & | \\ & CH_2 \\ & | \\ & COOH \end{array}$$

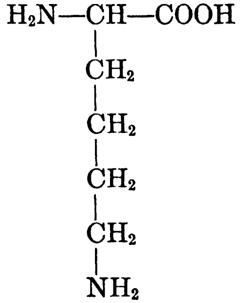
(glutamic acid 15.3%)

It also has two acids with two NH_2 groups. They are



$$\begin{array}{rl} H_2N- & CH-COOH \\ & | \\ & CH_2 \\ & | \\ & CH_2 \\ & | \\ & CH_2 \\ & | \\ & NH \\ & | \\ & C{=}NH \\ & | \\ & NH_2 \end{array}$$

(arginine 10.0%)



$$\begin{array}{rl} H_2N- & CH-COOH \\ & | \\ & CH_2 \\ & | \\ & CH_2 \\ & | \\ & CH_2 \\ & | \\ & CH_2 \\ & | \\ & NH_2 \end{array}$$

(lysine 3.0%)

These suspended chains may be the side chains attached to a main polypeptide chain.

SALT LINKAGES

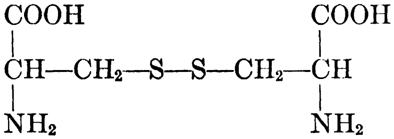
Now we must recall the very simple chemical reaction that takes place between an amine and an acid. The amine, with NH_2 group, is basic, so that the result of this reaction will be a salt, like an ammonium salt, in which the N group is positively charged and the acid radical is negatively charged.

$$R-NH_2 + HOOCR \longrightarrow RNH_3^{+}\ {}^{-}OOCR$$

The two molecules have been joined together by salt formation, and we may call this a salt linkage, in which the basic part and the acid part are held together by an electrovalent bond, the electrostatic attraction between positively and negatively charged ions. Now consider two main peptide chains side by side. On one chain there are arginine and lysine side chains with their free NH_2 groups; on the other chain there are glutamic and aspartic acid side chains with their free COOH groups. If the basic and acidic ends of these chains are close enough, they will neutralize each other and form a salt, like an ammonium salt. One part of this salt will be positively charged, the other part negatively charged, and the two parts will be held together by an electrovalent bond. The important thing is that, by this simple chemical reaction, one long chain has been linked to another long chain parallel to it. This is the salt linkage in wool, one of the types of cross-linkages that bind parallel chains together.

THE CYSTINE LINKAGE

The formula for cystine is:



$$\begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{CH}\\ |\\ \mathrm{NH_2}\end{array}\!\!-\mathrm{CH_2-S-S-CH_2}-\!\!\begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{CH}\\ |\\ \mathrm{NH_2}\end{array}$$

This is one of the most important constituents of wool and is closely associated with the characteristic behavior of wool. Note that it is both a dicarboxylic and a diamino acid. Let us consider how this amino acid might be placed in the protein of wool fiber. It is improbable that the two sulfur atoms are in the main peptide chain of wool, because this disulfide linkage is known to be easily ruptured. If the two sulfur atoms formed a part of the main chain of wool and other hair fibers, they would not have the properties that we know them to have. On the other hand, there is a fundamental probability that cystine forms a cross-linkage between the main polypeptide chains of wool, and that variations in the sulfur content of wool are due to variations in the number of such cystine cross-linkages. This idea was first proposed by Astbury and Street.[11]

If we accept these arguments, we must assume that the COOH and NH_2 groups of cystine have been incorporated in the main peptide chains of wool by condensation with the same groups of other amino acids, and that one pair of these groups is in one chain and the other pair is in another chain adjacent to it, as shown in Figure 2. There is quite a difference between this type of cross-linkage and the salt linkage. In the cystine linkage we have covalent bonds, and in the salt linkage electrovalent bonds. The covalent bonds are more resistant than electrovalent bonds to stretching and the action of water.

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[11] *Trans. Roy. Soc. (London)*, **A230**, 333 (1931).

In a very brief summary of the factors involved in the structure of wool protein we may say that (1) it consists of long polypeptide chains of condensed amino acids lying more or less parallel lengthwise of the fiber; (2) side chains lie between the main chains, some of which constitute cross-linkages; (3) dicarboxylic and diamino acids in side chains can neutralize each other to form salts which act as linkages between chains; and (4) cystine forms a covalent linkage between chains. We may thus consider wool as a very complex network of polypeptide chains linked together by covalent and electrovalent bonds, of which the cystine linkage is the most important; in fact, many of the characteristics of wool are dependent on this bond.

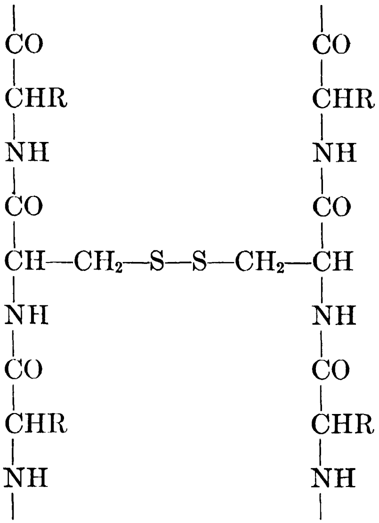

FIGURE 2.

We shall now attempt to picture all these factors in one structural formula which will show the three structural features of wool: main peptide chains, salt linkages, and cystine linkages. (See Figure 3.)

Harris, Mizell, and Fourt[12,13] give a good résumé and point out

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[12] *Am. Dyestuff Reptr.*, **31**, 376 (1942).

[13] *Ind. Eng. Chem.*, **34**, 833 (1942).

the connection between these structural features and some of the physical properties of wool. Wool consists of long polypeptide chains of condensed amino acids in a folded form which permits exceptional elongation. The application of tension will increase the orientation of these long chains and thus increase the strength,

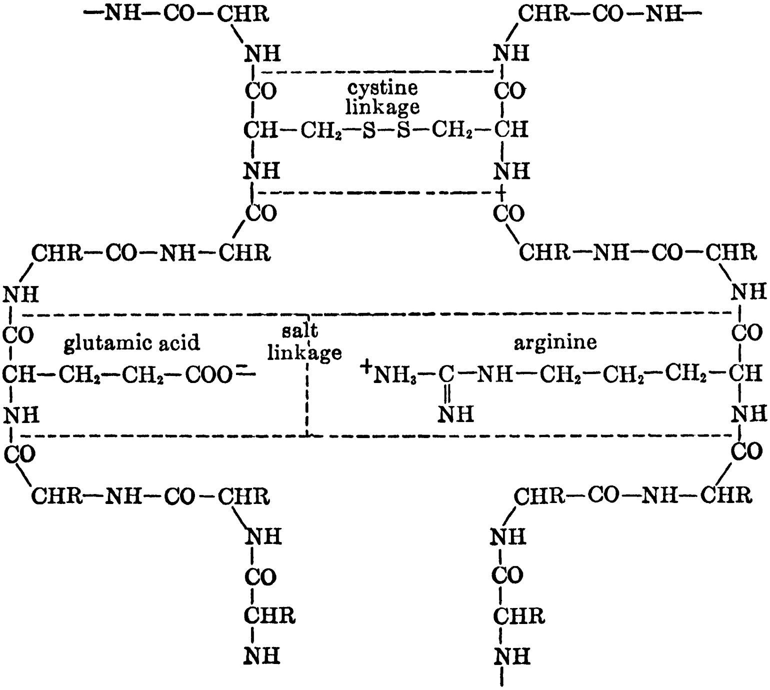

FIGURE 3.

but at the expense of elasticity. Part of the strength of wool is due to the existence of hydrogen bonds between molecular chains. Extending from the main polypeptide chains are side chains of varying sizes, and the side chains constitute about 50% of the weight of wool (as compared with 35% for silk), which means that there is little chance for a close packing of parallel chains. This reduces the chances for hydrogen bonding and thus contributes to the low tensile strength of wool. Cross-linkages increase the strength of wool, but if the degree of cross-linking is greatly increased, the fiber is less elastic. However, the long-range elasticity of wool is not entirely dependent on the cross-links. The elastic recovery of wool is probably due to the flexibility of the long folded chains and their ability to recover from the stretched form to the relaxed folded form; for this there must be a proper balance of cross-linkages.

Chemical Properties of Wool

REACTION OF WOOL WITH WATER

Wool is insoluble in water, and yet some profound changes take place when wool is treated with water under different conditions. There are three types of such changes, a change due to physical causes, a change in physical properties caused by chemical reaction, and a purely chemical change.

We are well aware that wool will felt and mat when agitated in hot water. This is mostly a physical reaction in which the epidermal scales of wool take part (page 257).

We also know that wool loses some strength when it is wet, and that it will stretch more easily when wet and still more easily when immersed in hot water. Furthermore, if wool is stretched or deformed and held in such condition while it is steamed, it will be set and will retain the new form for a considerable length of time. These two physical changes are the result of chemical reaction. Recall the probability of salt linkages in wool protein, which serve to hold adjacent chains together. Note that this salt is a salt of a weak base and a weak acid, one which should therefore be hydrolyzed by water, the extent of hydrolysis increasing with the temperature. If some of the salt linkages of wool are hydrolyzed, they are broken. Since these linkages contribute something to the strength of wool and offer some resistance to stretching, any rupture of such linkages would make the fiber a little weaker and allow it to be stretched more easily. If wool is stretched and steamed, many of these linkages are broken, but when the wool is cooled and dried in its stretched form, salt linkages are again formed, but in new positions, so that they help to hold the fiber in its new shape.

If wool is boiled in water at 130° C under pressure it becomes weak and brittle, and if boiled at 150° C under pressure it will be dissolved. Under these unusual conditions the wool protein is hydrolyzed by water to such an extent that its fibrous form is lost and it is split into amino acids.

THE ACTION OF ACIDS ON WOOL

We shall discuss the action of dilute and concentrated mineral acids and of organic acids on wool. Wool is not very sensitive to dilute acids; in fact, when wool yarn is dyed with acid dyes, it is boiled in a bath containing sulfuric acid. However, dilute acids such as HCl, H_2SO_4, HNO_3, and chromic acid (CrO_3) are absorbed by wool in such a way that a certain amount of the acid cannot be rinsed off. Such acidified wool will come up a slightly deeper shade from a bath of an acid dyestuff.

It is interesting to note that almost all kinds of wool absorb and retain the same amount of acid. For example, 100 gm of dry wool will absorb the equivalent of 80 ml of 1 *N* HCl. Speakman has suggested that this means that the basic amino acid content of all wools is the same. However, such a conclusion is debatable because other factors may enter into the problem. There are at least three possible ways in which acids can be retained by wool: (1) they may be held in the capillaries of the fiber by capillary forces, (2) they may be absorbed on the surfaces of micelles and held there by secondary valence forces, or (3) they may react chemically with free NH_2 groups and be held by primary valences. Most evidence seems to favor the last reason, and there are two methods of explaining it. Speakman[14] explains it by assuming that the salt linkages of wool are broken by mineral acids, liberating free NH_2 groups which are immediately neutralized by the mineral acid. This is logical because we know that the action of a strong acid on the salt of a weak acid liberates the weak acid. For example, acetic acid is liberated when ammonium acetate is treated with HCl.

$$CH_3COONH_4 + HCl \longrightarrow CH_3COOH + NH_4Cl$$

We might think of this as a two-step reaction, first the splitting of CH_3COONH_4 into CH_3COOH and NH_3, followed by the reaction between NH_3 and HCl to form NH_4Cl. An analogous situation is found in wool where there are salt linkages like ammonium acetate, and these should react with HCl as shown below.

$$W{-}COO^{-}\ {}^{+}H_3N{-}W + HCl \longrightarrow W{-}COOH + W{-}NH_3Cl$$

W—COOH is like acetic acid, and $W{-}NH_3Cl$ is like NH_4Cl.

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[14] *J. Textile Inst.*, **32**, T83 (1941).

Harris, Neville, and Fritz[15] presented evidence in support of the chemical combination of acids based on a study of iodine absorption values. Iodine is known to react with the free NH_2 group of amino acids, and therefore the absorption of iodine by wool is a measure of free NH_2 groups. The wool they worked with had an iodine absorption value of 14.1. After immersion in 1 N H_2SO_4, the value dropped to 2.6, which shows that many free NH_2 groups of wool can be blocked by acid. After very thorough rinsing an iodine value of 9.6 was obtained; this remained constant. Even though the acid cannot be rinsed off, it can be neutralized. This was demonstrated by treating acidified wool with Na_2CO_3 before determining the iodine value. After the soda rinse the iodine value was 14.1, the same as the original value.

The action of concentrated mineral acids on wool can be easily stated. Concentrated H_2SO_4 causes wool to swell, gelatinize, become rubbery, and finally be completely destroyed. Concentrated HCl does the same thing over a somewhat longer period of time. Concentrated HNO_3 forms a characteristic yellow color with wool. This yellow substance has been called xanthoproteic acid.

The action of organic acids on wool is similar to that of dilute mineral acids; that is, they are absorbed from dilute solutions. The action of tannic acid on wool changes its dyeing property. Wool will absorb tannic acid as it does the other organic acids, but it is easily washed out. However, tannic acid can be fixed on wool by immersing the acid-treated wool in a bath of tartar emetic. This produces a complex antimony tanrate, which is insoluble. Tannined wool has very little affinity for acid and direct dyes, but has increased affinity for basic dyes. It can be used in resist methods for dyeing wool. Tannined and untreated yarns can be woven together in any desired pattern, and then the cloth dyed in one bath. The two sets of yarns will be dyed differently.

Wool is often treated with dilute mineral acid in a process known as carbonizing. When raw wool is scoured small bits of grass, burrs, etc., are left on it. In order to remove these the wool may be immersed in dilute sulfuric acid, dried at room temperature, and then baked at 120° C. This chars the vegetable matter so that it can be dusted out. When mixed goods are converted into wool shoddy the cotton can be removed by a similar treatment.

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[15] *Am. Dyestuff Reptr.*, **23**, 323 (1934).

THE ACTION OF ALKALIES ON WOOL

Wool is quite sensitive to alkalies, especially the caustic ones, NaOH and KOH. Carbonated alkalies, such as Na_2CO_3, do not harm wool if used properly, so that we find soda being very generally employed in wool scouring and finishing. However, soda must not be used on wool at high temperatures. Ammonia is a very mild alkali and does not harm wool, even at the boiling point, for some time.

The action of caustic alkali on wool is very peculiar. Dilute solutions, 5% NaOH, are quite harmful to wool, causing a considerable loss in strength and elasticity. As the strength of NaOH increases, the same harmful effect is found to be true until a concentration of about 15% NaOH is reached, after which the amount of damage decreases. Crepon effects on cloth can be obtained by passing a wool-cotton union through a 30% solution of NaOH. You already know that this will cause a large amount of shrinkage (mercerization) in the cotton yarns, but it does not affect the wool yarns if the temperature and time are kept down. The danger to wool is not in the 30% NaOH solution, but in what may happen after the wool comes out of the solution. The next step would be a washing operation in which the NaOH is diluted, but when the dilution goes down to 15% the wool will be damaged. The proper use of large amounts of water and rapid neutralization with dilute acid will minimize such damage.

If the concentration of NaOH is increased to 35 or 40%, the reaction with wool is still more unexpected. It is found that the wool has gained about 30% in strength, is whiter, has a higher luster, and a silky scroop. It is sometimes called mercerized wool. This effect is not so noticeable when individual fibers are thus treated, so that it is possible that the increased strength of wool yarn is due to a gelatinization of the surface with increased cohesion.

The change in tensile strength with variation in NaOH concentration is shown in Table 44. The strength of the original yarn was 610 gm, and time of treatment was 5 minutes at 10° C.

Now let us look at what may happen to the structure of wool protein when it is treated with NaOH. Strong caustic alkali may act in three different ways: (*a*) it may hydrolyze the main polypeptide chains of protein, breaking them down into sodium salts of amino acids; (*b*) it may rupture salt linkages; (*c*) it may hydrolyze cystine linkages.

The hydrolyzing of peptide chains would require a fairly radical treatment. For example a 5% NaOH solution will completely dissolve wool in a few minutes at the boiling point. This involves total destruction of the wool. We may take advantage of this reaction in analytical work. If a mixture of wool and cotton is boiled with 5% NaOH, the wool will dissolve but the cotton will not be affected, and it may be washed, dried, and weighed, to determine the percentage of cotton in the sample. If the NaOH solution is carefully acidified with HCl, a white solid will be precipitated. This material is a mixture of amino acids which has been called lanuginic acid.

TABLE 44

Strength of Wool Yarn after Alkali Treatment

Per Cent NaOH	Strength, gm	Per Cent Change in Strength
0	610	......
3.0	510	−16.4
5.5	475	−22.1
8.0	250	−59.0
11.0	180	−70.5
15.0	95	−84.5
18.0	200	−67.2
22.0	240	−60.6
30.0	580	−4.9
35.0	770	+26.2
38.0	815	+33.6

The alkaline rupture of salt cross-linkages in wool protein is based on a very simple reaction. We found that acid splits salt linkages because it liberates the weak acid, i.e., it is the action of a strong acid on the salt of a weak acid. The action of caustic alkali is the same thing except that it liberates a weak base. Remember that the salt cross-linkages in wool are salts of weak bases and weak acids. Therefore the weak bases will be liberated when they are treated with NaOH.

$$\text{W—COO}^{-}\ {}^{+}\text{H}_3\text{N—W} + \text{NaOH} \longrightarrow \text{W—COONa} + \text{H}_2\text{N—W} + \text{HOH}$$

The attack by caustic alkali on the cystine linkages of wool is accompanied by considerable loss in sulfur (the so-called labile sulfur). Crowder and Harris[16] treated wool with 0.05 *N* NaOH at 65° C for various lengths of time, and obtained some astonishing and significant results. The surprising thing is that wool should be changed so much by such a mild treatment. The NaOH solution is so very dilute, only 2 gm in a liter, a 0.2% solution, and yet in only 15 minutes at 65° C the wool lost over 20% of its sulfur and about 50% of its cystine. It also lost 2.27% of its weight. The significant thing is that part of the S is converted into a soluble form (and therefore removed during washing), and part of it is stable. Crowder and Harris proposed that the first step in the alkaline degradation of wool is the hydrolytic rupture of the cystine linkage (the disulfide linkage) to form two things, in one of which the S is labile, and in the other, stable. The initial alkaline hydrolysis of the cystine linkage of wool results in a sulfhydryl (in which the sulfur is not labile), and a sulfenic acid (from which the sulfur is easily split off).

$$\mathrm{W{-}CH_2{-}S{-}S{-}CH_2{-}W + HOH}$$
$$\xrightarrow{\mathrm{NaOH}} \underset{\text{(sulfhydryl)}}{\mathrm{W{-}CH_2{-}SH}} + \underset{\text{(sulfenic acid)}}{\mathrm{W{-}CH_2{-}S{-}OH}}$$

The sulfenic acid is unstable and is immediately decomposed into H_2S and an aldehyde

$$\mathrm{W{-}CH_2{-}S{-}OH \longrightarrow W{-}CHO + H_2S}$$

The H_2S would of course dissolve in the alkaline medium to form Na_2S. The presence of an aldehyde is confirmed by the intense color formed with Schiff's reagent.

We shall find later that such damage to wool can be repaired by certain treatments which will form new cross-linkages.

From a practical point of view, it should be apparent that wool is very sensitive to the action of dilute caustic alkalies, that the reaction is one of degradation, and that considerable damage is done in a short time under mild conditions. Every effort should be made to keep wool away from caustic alkalies. One way in which the housewife might fail in this is by the use of low-grade soaps. Some soaps contain free caustic alkali that will be very harmful to wool. Only the best grade of neutral soap should be used to wash wool, and the temperature should be kept down.

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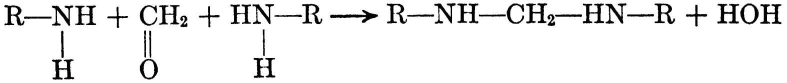
[16] *Am. Dyestuff Reptr.*, **25**, 264 (1936).

THE FORMATION OF NEW CROSS-LINKAGES

The purpose of finding out how to produce new cross-linkages in wool is to stabilize it against the action of alkalies, oxidizing and reducing agents, and other agencies such as light. We have found that wool is not very sensitive to dilute mineral acids because it does not seem to be harmed during the carbonizing operation. And yet some incipient damage may be done, which will not show up until the material is laundered. Laundering treatments are always slightly alkaline, and even this weak alkalinity may bring about damage which would not normally be caused by laundering. The same is true of the effect of oxidizing agents. Slight damage caused by them may not become apparent until the material comes into contact with alkali later. It would be highly desirable if we could discover some way to stabilize or protect wool so that it would not be so sensitive to these various agencies.

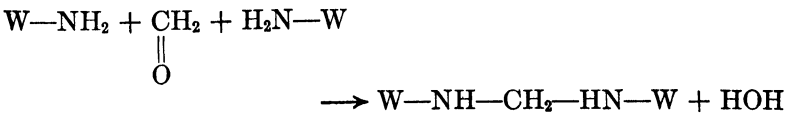
This problem has been attacked from the point of view of producing new cross-linkages which will be more stable than those in native wool. This matter has been approached in two ways. In England, Speakman and other workers have produced new linkages by a direct treatment of wool with aldehydes and ketones. In this country, Harris and his associates have first reduced the wool and then produced a new linkage between reduced groups in adjacent polypeptide chains. Speakman works with free NH_2 groups in wool, and Harris works with disulfide linkages.

It is well known that primary amines will condense with formaldehyde to form compounds in which two nitrogens are joined through a CH_2 group.



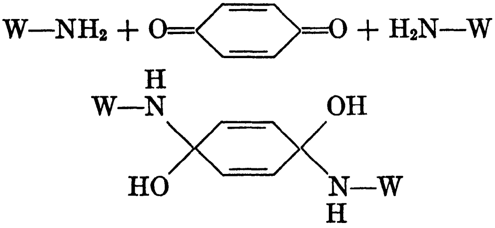
$$\mathrm{R{-}\underset{\substack{|\\ H}}{N}H + \underset{\substack{\|\\ O}}{C}H_2 + H\underset{\substack{|\\ H}}{N}{-}R \longrightarrow R{-}NH{-}CH_2{-}HN{-}R + HOH}$$

A similar reaction might be expected to take place between formaldehyde and the free NH_2 groups of wool, forming a cross-link with a CH_2 group in it.



$$\mathrm{W{-}NH_2 + \underset{\substack{\|\\ O}}{C}H_2 + H_2N{-}W \longrightarrow W{-}NH{-}CH_2{-}HN{-}W + HOH}$$

It has been found that wool is strengthened by a formaldehyde treatment. Speakman[17] applied a modification of this reaction to the introduction of new cross-links in wool by using benzoquinone which is a cyclic diketone. This reaction is not a condensation but simply the addition of an amino group to a ketone.



Speakman and Peill[18] found that successful results depend upon *p*H. The best conditions for formaldehyde treatment are at *p*H from 6 to 7, whereas the quinone cross-linkage is best formed at *p*H from 4.7 to 5. On either side of these values the increase in strength of wool is not so great.

Recall the rupture of salt linkages caused by the action of caustic alkali, in which one product is a free NH_2 group. Such damage might even be repaired by a formaldehyde treatment.

The procedure used by Harris is to break the disulfide bond and then build a new one which is more resistant. Patterson, Geiger, Mizell, and Harris,[19] and Geiger, Kobayashi, and Harris[20] reduced the disulfide linkage with thioglycellic acid, $HSCH_2—COOH$, to split the cystine linkage and form two sulfhydryls.

$$\text{W—S—S—W} + 2\text{HSCH}_2\text{—COOH} \longrightarrow 2\text{W—SH} + (\text{SCH}_2\text{COOH})_2$$

The sulfhydryls can be reacted with dihalogen compounds, such as $BrCH_2Br$ or $Br—(CH_2)_3—Br$.

$$\text{W—SH} + \text{Br—(CH}_2)_3\text{—Br} + \text{HSW} \longrightarrow \text{W—S—(CH}_2)_3\text{—S—W} + 2\text{HBr}$$

We now have two adjacent peptide chains joined together by a new cross-linkage,

$$\text{—S—CH}_2\text{—CH}_2\text{—CH}_2\text{—S—}$$

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[17] *J. Textile Inst.*, **32**, T106 (1941).

[18] *J. Textile Inst.*, **34**, T70 (1943).

[19] *J. Research Natl. Bur. Standards*, **27**, 78 (1941).

[20] *Ind. Eng. Chem.*, **34**, 1938 (1942).

which is much more resistant than the —S—S— linkage. This is evidenced by the fact that wool so treated is only about one-third as soluble in alkali as untreated wool. At no time during this treatment has the fibrous structure of wool been affected.

Recall that sulfhydryls are formed when the cystine linkage is damaged by weak alkali. It is possible that such damage might be partially repaired by treating the damaged wool with $Br—(CH_2)_3—Br$.

Brown and Harris[21] have reported an improvement on the process for rebuilding new stable cross-links in wool after the cystine linkages have been broken by the action of a reducing agent. The new process involves only one step, in which the wool is immersed in a bath containing both the reducing agent and the reagent that makes the new linkage. They use inorganic reducing agents such as sodium sulfoxylate formaldehyde, $NaHSO_2—CH_2O—2H_2O$, or the corresponding zinc compound, or sodium hydrosulfite, $Na_2S_2O_4$. Compounds suitable for rebuilding the new linkage are dihalides (as previously used), formaldehyde, or glyoxal, CHO—CHO. In applying the process, the cross-linking reagent and the reducing agent are mixed and buffered to a *p*H of about 7 and heated to 80 to 90° C, and the wool is immersed for 1 to 1½ hours. The one-step principle, on which the treatment is based, is that, as quickly as a disulfide linkage is broken to form sulfhydryls, the cross-linking reagent acts immediately to rebuild a new linkage. The concentration of the reducing agent is not important in the presence of the cross-linking reagent; that is, an excess does no harm, whereas, in the absence of a reagent such as formaldehyde, wool is damaged by alkaline solutions of sulfoxylate or hydrosulfite. The cystine content of wool is about 0.0005 mole per gram of clean wool. This figure determines the amount of dihalide to be used, as they react in the ratio of 1 : 1.

It is extremely interesting to note that, whereas this process for rebuilding cystine linkages in wool was the result of a fundamental research aimed at improving the quality of wool, the first large-scale use of it was in the wool shoddy industry. One of the steps in the manufacture of wool shoddy is the stripping of dyes from the scrap wool. Sodium hydrosulfite has been one of the most used stripping agents, but this treatment has always been accompanied by a certain unavoidable amount of degradation of the wool, brought about by the alkalinity of the stripping bath. In 1949 one large mill experimented with the addition of a cross-linking reagent to the stripping bath. The hoped-for result was obtained: the dyes were stripped, cystine linkages were ruptured, and new cross-linkages were introduced. Thousands of pounds of wool are being processed each week in this way. The quality of such wool shoddy is equal to, or better than, that of the used wool before it is reclaimed.

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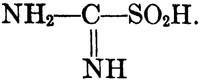
[21] *Ind. Eng. Chem.*, **40**, 316 (1948).

Other reducing agents which are claimed to be better than those already mentioned are covered by patents.[22,23] Among these reducing agents are symmetrical acetyl thiomethyl urea, $(CH_3CO\text{—}SCH_2\text{—}NH)_2CO$, and formamidinesulfinic acid.  $NH_2\text{—}\underset{\underset{NH}{\|}}{C}\text{—}SO_2H$. Another patent[24] claims the formation of cross-links without first breaking the disulfide linkages. This is accomplished by treating wool with styrene in ether solution with iodine as a catalyst.

ACTION OF REDUCING AND OXIDIZING AGENTS: BLEACHING

Wool is very little affected by reducing agents such as sulfurous acid (SO_2), and as the coloring matter of wool is decolorized by SO_2, it is widely used for bleaching wool. However, the white obtained is not very permanent, but a hydrogen peroxide bleach gives a permanent white. For this reason a combination of the two bleaching agents is generally used.

In commercial practice, wool is bleached with H_2O_2 slightly on the alkaline side (*p*H of about 9), with time and concentration varying with several factors. The wool is then washed and immersed for a short time in dilute H_2SO_4 (1 to 2%) containing small amounts of dissolved SO_2 (sulfurous acid), after which it is washed thoroughly.

Harris and his associates[25] made an extensive study of the relation between extent of oxidation and the alkali solubility of the resulting wool. They studied both bleaching and chlorinating agents and suggested alkali solubility as a good control method

[22] U.S. Patent 2,403,906 (1946).

[23] U.S. Patent 2,403,937 (1946).

[24] U.S. Patent 2,406,958 (1947).

[25] *J. Research Natl. Bur. Standards*, **15**, 63 (1935); **16**, 301, 309, 475 (1936).

for mill use. They definitely established the fact that, whereas there may be no immediate evidence of damage by oxidation, the sensitiveness to alkalies is increased, so that serious damage may be done in laundering, where alkaline treatments are the general rule. For the control of oxidation operations, Harris and his co-workers recommend treating a sample with 0.1 N NaOH at 65° C for 1 hour. Unoxidized wool will lose from 11.5 to 13% weight by such a treatment. All oxidized samples will show a greater loss in weight.

THE SHRINKPROOFING OF WOOL

We have discussed (page 257) the factors that contribute to the felting property of wool and have learned that felting is always accompanied by shrinkage. We are now concerned with these same factors in reverse; that is, what we can do to wool yarn so that it can be knitted into sweaters or socks that will show a greatly reduced shrinkage when washed, or how we can treat a wool cloth so that it will not shrink as much as usual? It must be understood that a complete absence of shrinkage cannot be obtained, but if we can get a reduction of 30 to 60% in shrinkage it is well worth the effort. The use of the word shrinkproofing is probaly incorrect, and we should think of the treatments we are about to discuss as methods for making wool shrink-resistant or methods for the dimensional stabilization of wool.

Two of the several factors involved in felting stand out as points of attack in the problem of making wool shrink-resistant. They are the scaliness of the cuticle of the wool fiber, and the elastic property of wool, which depends on the unfolding and contracting of the long polypeptide molecular chains in wool. If the first can be made inoperative and the second modified without too much loss of such desirable properties as softness, strength, loftiness, etc., a great advance will have been made. No single treatment can attain both these objectives, so we find that methods for making wool shrink-resistant can be divided into two groups: (*a*) those methods which aim at an attack on the cuticular surfaces and are based on actual chemical reactions in which wool takes part, and (*b*) those methods which are more or less mechanical and are based on the deposition of substances on or within the wool fibers so as to mask the surface scales or affect the unfolding and contractile properties of wool.

There are three general chemical methods for producing nonshrinkable wool: (*a*) treatment with oxidizing agents (usually chlorine compounds), (*b*) the alcoholic alkali method (Freney-Lipson method), and (*c*) the use of enzymes.

THE CHLORINATION OF WOOL

The use of various oxidizing agents for shrinkproofing wool is discussed by Alexander.[26] He mentions such reagents as $KMnO_4$, fluorine, alkaline hypochlorite, aqueous chlorine (acid medium), dry Cl_2 gas, Cl_2 in CCl_4 medium, aqueous bromine, or Br_2 in CCl_4 medium. Other chlorine compounds investigated are sulfuryl chloride, SO_2Cl_2; chlorosulfonic acid, $ClSO_2OH$; and *p*-toluenesulfondichloroamide, $CH_3—C_6H_4—SO_2NCl_2$. However, from a practical standpoint only two oxidizing treatments are satisfactory for shrinkproofing wool. They are the wet and dry chlorination methods.

A typical commercial method for the chlorination of wool would be to wet out the wool at room temperature and then add 1% borax, mix well, and add sufficient stock solution of bleach (hypochlorite) to make a 3 to 4% available chlorine mixture. The temperature may then be raised to 40 to 45° C. After the proper amount of chlorination has taken place, the bath is drawn off and the wool is treated with 1% $NaHSO_3$ (an anti-chlor), which destroys residual chlorine left in the wool. Finally, the wool is washed thoroughly.

Such a treatment will attack the surface scales of wool, causing a swelling and gelatinizing so as to coat the surface with a covering, thus preventing felting. The objection to this method is that it is difficult to stop the chlorination reaction at the proper point. Elliot and Speakman[27] have proved that the chemical action of chlorine on wool is the rupture of the cystine (disulfide) linkage. Phillips[28] points out that chlorine reacts with wool very rapidly, and thus the surface portions of the wool may be chlorinated too much before the interior portions are attacked. Thus the exposed fibers of a yarn or cloth will absorb most of the chlorine from the chlorinating bath and become weakened. There is also considerable yellowing of the wool when it is chlorinated. A great amount of research work has been carried out in an effort to solve the problem of fiber damage during chlorination. It has been suggested that the chlorinating reagent be added in portions, and more slowly, to the treatment bath. Other proposals are that the pH of the bath should be more carefully controlled. Phillips[28] states that at a pH of 2.0 about 95% of the chlorine is removed from the bath in 2 minutes, whereas at a pH of 8.0 only 30% of it is removed in the same length of time. The Alrose Chemical Company controls the Protonized wool shrinkage control process. This process slows up the chlorination of the wool by the use of a chemical which will react with chlorine and then release it to the wool more slowly. This substance is sodium sulfamate, $NH_2—SO_2—ONa$, which reacts with hypochlorous acid to form mono- and dichlorosulfamates,

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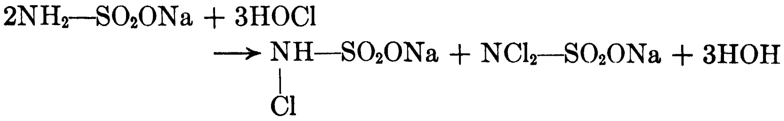
[26] Society Dyers and Colourists, *Fibrous Proteins Symposium,* 199–202, May 1946.

[27] *J. Chem. Soc.*, 641 (1940).

[28] *J. Textile Inst.*, **37**, P302 (1946).



$$\mathrm{2NH_2—SO_2ONa + 3HOCl \longrightarrow \underset{\underset{Cl}{|}}{NH}—SO_2ONa + NCl_2—SO_2ONa + 3HOH}$$

These chlorosulfamates are stable in acid medium, but, in the presence of wool, chlorine is released slowly and uniformly, and the chlorination of the wool proceeds in an orderly and reproducible manner, with very little damage to the wool.

THE ALCOHOLIC ALKALI PROCESS

This process (the Freney-Lipson method, 1939) consists of the following steps: (1) the dry wool is immersed in a bath containing 2.8% KOH and 1% glycerin in methyl alcohol (containing 3 to 5% water) at 80° F for 10 minutes; (2) it is steeped in 1% H_2SO_4 for 4 minutes at room temperature; (3) it is rinsed with water; (4) it is rinsed with modified soda; and (5) it is again rinsed with water.

Tests made by the U.S. Army Quartermaster General's Office[29] on socks treated by this method showed extremely good results.

Modifications of this method are controlled by Tootal-Broadhurst Lee Company, Ltd. (England), under patents[30] that claim the treatment of wool with NaOH in an alcohol, such as butyl alcohol, which will not dissolve the alkali completely. Shrinkage is reduced enormously.

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[29] *Am. Dyestuff Reptr.*, **34**, 68 (1945).

[30] U.S. Patents 2,367,273 and 2,401,479 (1946).

THE ENZYME METHOD

The use of papain for making wool shrink-resistant was patented by Phillips and Middlebrook[31] in England. When wool is immersed in solutions of papain, it is solubilized or digested, and thus we should expect such a treatment to destroy the free edges of the scales and reduce shrinkability. Phillips[32] points out that this digestive reaction is very slow, but in the presence of 1% sodium bisulfite solution papain is intensely active. The $NaHSO_3$ is supposed to break down the disulfide linkages of wool and form sulfhydryl groups. It also probably activates the papain so that the degradation of the wool surfaces is enhanced. However, tests made by the Quartermaster General's Office showed that the modification of the wool was excessive compared with the shrinkproofing efficiency.

The Chlorzyme process first chlorinates wool and then treats it with papain. It is claimed that the enzyme will remove the slightly harsh and dry surface left after chlorination, and yield a product which is soft and has a silklike luster.

SHRINKPROOFING WOOL WITH RESINS

Two types of resins can be used for making wool shrink-resistant when washed. One is the condensation product of urea with formaldehyde, and the other is a similar product obtained by condensing melamine with formaldehyde. Under varying conditions, the latter reaction yields a series of methylolmelamines (see page 204). These melamine resins were developed by the American Cyanamide Company, which controls their manufacture. The efficiency of melamine resins for controlling the shrinkage of wool appears to be much greater than that of the urea-formaldehyde resins. Dudley and Lynn[33] state that four or five times as much urea-formaldehyde resin as melamine resin is required to obtain the same amount of shrinkage stabilization. Resins obtained by the condensation of phenol with formaldehyde can be used to make wool shrink-resistant, but the color is too dark.

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[31] British Patent 513,919 (1938).

[32] *J. Textile Inst.*, **37**, P302 (1946).

[33] Society Dyers and Colourists, *Fibrous Proteins Symposium*, 215–220, May 1946.

All of these resins are thermosetting, which means that when they are properly heated (cured) they polymerize to infusible masses that are unaffected by further heating. In general the method involved in treating wool with resins is to impregnate the goods with a water solution of the resin, run through squeeze rollers, dry rapidly, and then heat to a fairly high temperature in order to polymerize the resins. The shrinkproofing result may be due to one (or both) of two factors: (1) the surface of wool fibers may be strengthened and the scales made inoperative to frictional effects by the polymerization of the resin on the surface; or (2) the resin may penetrate into the interior of the wool fiber before polymerization starts, in which case the impedance offered to the unfolding and contracting of the molecular chains of wool would decrease its felting property and thus its shrinkage. Johnstone[34] states that microphotographs of melamine-treated wool indicate that the resin is perhaps deposited within the cortical cells and therefore affects the intrinsic elasticity of the wool.

Among the many melamine-formaldehyde resins is one that has been devised for and is especially suitable for controlling the shrinkage of wool. It is known as Lanaset resin. It is not a straight melamine resin but a methylated methylolmelamine, made by treating the melamine-formaldehyde condensate with CH_3OH.[35] It is put on the market as an almost colorless syrup containing 80% solids. A resin like this is applied to wool from a bath which contains some wetting agent (to give more uniform impregnation) and an accelerator or catalyst, such as aluminum, ammonium, or zinc sulfate. The wool is simply immersed in the bath and then squeezed out until it retains about 80% moisture, after which it is dried and then heated in order to polymerize the resin. The time of heating depends on the temperature. For example, it would be heated for 45 minutes at 230° F, but for only 6 minutes at 300° F. This heating, or curing, polymerizes the resin to an infusible, insoluble form. After curing, the goods should be thoroughly washed to remove any accelerator left over, and any surface or uncured resin.

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[34] *Am. Dyestuff Reptr.*, **33**, 301 (1944).

[35] U.S. Patent Reissue 22,566; Canadian Patent 419,781 (1944).

The extent of shrink resistance of Lanaset-treated wool cloth reported by Johnstone is shown in Table 45.

TABLE 45

SHRINKAGE OF LANASET-TREATED WOOL

Per Cent Resin in Wool	Shrinkage after Washing for		
	15 min	30 min	60 min
0	11.1%	18.0%	29.2%
2.5	4.0	5.5	12.5
5.0	2.1	3.5	5.5
10.0	1.4	2.1	2.4

A good tabulation of resins suitable for making wool shrink-resistant is given by Rabold,[36] in which he lists the types of resins, together with their properties and uses.

THE SETTING OF WOOL

Wool can be stretched or distorted to a new shape while it is subjected to the action of steam or is under a wet high temperature. If it is held in this new shape until it cools, it will retain the distorted form. It is then said to have been set, and this set is fairly permanent. Many commercial operations are based on this property of wool.

Speakman[37] discusses the structure of wool, the types of cross-linkages, and the part they play in the setting of wool. It is known that wool has a characteristic contractile property which is dependent on the cross-links that bind the parallel polypeptide molecular chains together. Because of the normal folded structure of wool (see page 260), it will recover its shape after it is stretched, and the cross-links must play an important part in the maintenance of this folded or relaxed condition. If the cross-links are ruptured, the wool could be distorted, but a loss in strength would accompany this rupture and distortion. However, we know that wool does not lose strength when it is properly set. Therefore, if the setting operation causes a rupture of cross-linkages, some new linkages must be produced in order to retain the normal strength. These new links must be formed by the reaction between two things, at least one of which was produced by the rupture of cross-linkages.

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[36] *Textile World*, **95**, 93 (1945).

[37] *J. Textile Inst.*, **27**, P231 (1936).

Speakman and Hind[38] studied the effect of *p*H on the extent to which wool can acquire a permanent set. At a *p*H of 1.0, it is very difficult to give wool a permanent set; at a *p*H of 4.4, there is the least possibility; and the best results are obtained at a *p*H of 9.2. This means that a slight alkalinity is necessary. Our knowledge of the chemical properties of wool tells us that strongly alkaline solutions would damage wool too much, even though they might fulfill the fundamental requirements of a setting agent. Speakman claims that steam alone will hydrolyze disulfide linkages to form a sulfhydryl and sulfenic acid, as shown by

$$\mathrm{W{-}CH_2{-}S{-}S{-}CH_2{-}W + HOH \longrightarrow \underset{\text{(sulfhydryl)}}{W{-}CH_2{-}SH} + \underset{\text{(sulfenic acid)}}{W{-}CH_2{-}SOH}}$$

where W represents a polypeptide chain. While the wool is in this relaxed condition it can be reshaped, and when held and cooled an entirely new and different cross-linkage is formed. This is produced by the action of sulfenic acid groups with free NH_2 groups on side chains of adjacent polypeptide chains. As these groups are basic, they would react with sulfenic acid to form a salt like an ammonium salt,

$$\mathrm{W{-}CH_2{-}S{-}OH + H_2N{-}W \longrightarrow W{-}CH_2{-}S{-}ONH_3{-}W}$$

which would then lose water to form $\mathrm{W{-}CH_2{-}S{-}NH{-}W}$, so that the treatment amounts to a condensation reaction. Such free NH_2 groups would be found at the uncondensed end of units of lysine or arginine (diamino acids). These NH_2 groups might be free in the wool structure, or they may have been formed by the hydrolysis of salt cross-linkages, especially in a slightly alkaline medium.

On the other hand, setting conditions might split salt linkages, and then new salt linkages in new positions would be formed when the set wool is cooled. However, it is conceded that a rupture of cystine linkages is necessary for setting.

A high temperature is not necessary for setting if some reagent is used which will break disulfide linkages and yet not damage wool. Speakman[39] has patented a process, based on this premise, in which wool or hair is treated with solutions of 5 to 20% sodium bisulfite in 45% ethyl alcohol at room temperature for 15 minutes. The wool is then in a relaxed state with many cystine linkages broken, and it can be formed into a new shape. This shape can be made permanent by treating with an oxidizing agent such as H_2O_2 or a 10% alkali persulfate solution. This will destroy the bisulfite and permit new cross-links to be formed.

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[38] *J. Textile Inst.*, **36**, T19 (1945).

[39] U.S. Patent 2,351,718 (1944).

QUESTIONS

1. Make a sketch showing the structural parts of the wool fiber. Tell what role each part plays in the use of wool as a textile fiber.
2. What is the general degree of scaliness among fine, medium, and coarse wools?
3. What is the fulling or milling operation? Why is it done?
4. Why are long wools usually more lustrous than short wools?
5. What structural part of wool is associated with its waviness?
6. What is kempy wool?
7. Make a drawing showing how wool fibers grow out of the skin of sheep, and the location of glands that contribute most of the impurities in raw wool.
8. How is raw wool cleaned by the solvent process? How is it scoured? Explain how the two major impurities are removed from wool by this method.
9. What is suint? wool grease? lanolin?
10. What are the limitations on type of soap, temperature, agitation, and water in wool scouring?
11. What physical properties of wool make it such a highly prized textile fiber?
12. What is the length range of fine, medium, and coarse wools?
13. What is meant by saying that a particular wool is 60's quality?
14. What physical properties of wool contribute to its very good spinning quality?
15. What would be an average regain for wool? How does this compare with cotton and rayon?
16. What connection is there between humidity and the strength of wool yarns? between humidity and the count of wool yarns?
17. Discuss the various theories of the cause of wool felting.
18. What is the picture of the chemical structure of wool?
19. How are the adjacent polypeptide chains of wool held together (two types of cross-linkages)?
20. Show how each of these would be split by the action of alkalies.
21. Discuss two ways in which new cross-links can be put into wool.
22. Write a formula to illustrate a salt linkage. How would it react with a strong acid (HCl) and a strong base (NaOH)?
23. How does wool behave with dilute and concentrated mineral and organic acids?
24. Why is wool carbonized? How is it done?
25. Compare the action of wool and cotton with caustic alkalies.

26. Why is wool so easily damaged by caustic alkali?

27. Compare the effect of 3% NaOH and 28% NaOH on wool for short periods of time at low temperatures. If wool were treated with 38% NaOH and then rinsed with water so as to remove the alkali, what would happen?

28. How can cross-links be ruptured by the action of NaOH? What are the products of the alkaline rupture of cystine linkages?

29. Write equations to illustrate the formation of a new methylene cross-linkage in wool by means of formaldehyde.

30. What is the Harris method for introducing new cross-linkages into the cystine region of wool?

31. What two important physical properties of wool must be modified or made inoperative if any shrinkproofing treatment is to be successful?

32. How can wool be made shrink-resistant by means of chlorine compounds?

33. What is the Freney-Lipson method for making wool shrink-resistant?

34. What are the objections to the chlorination of wool?

35. How can enzymes be used for shrinkproofing wool?

36. Which resin, urea-formaldehyde or melamine-formaldehyde, is considered to be more practical for making wool shrink-resistant? How are these resins applied to wool cloth?

37. Explain how it is possible for wool to be set.

10 · Silk

Silk is a continuous protein filament extruded by the silkworm when it spins the cocoon in which it spends the chrysalis stage of its life cycle. Although silk is produced by more than one genus of the order of Lepidoptera, only one is of major importance. This is the genus Bombyx, the principal species of which is the *Bombyx mori.* This is the worm that feeds on the leaves of mulberry trees, and its silk is often called mulberry silk to distinguish it from the wild silks.

The life story of the silkworm is a short and strange one. Eggs are laid by the silk moth, an animal that is without a mouth and therefore does no eating. It lives for only two to four days, during which its sole function is to reproduce by mating and laying eggs. The female moth lays about 500 eggs. The incubation time for the eggs is 8 to 12 days, after which a caterpillar is hatched. It weighs about 5 mg and is about 2 to 3 mm long. For 20 to 30 days after hatching, the worm does practically nothing but eat mulberry leaves. During this eating period the worm gains about ten thousandfold in weight and grows to be from 5 to 9 cm long. It is then ready to enfold itself in the cocoon which it spins around itself. The spinning is done quite rapidly, considering that the worm spins from 3000 to 4000 yd of filament in 4 or 5 days. It now enters the chrysalis, or pupa, stage during which a remarkable change takes place. The chrysalis is a hard, inert, almost lifeless thing which, after 10 or 12 days, changes into a moth. The moth cuts its way through the cocoon and is then ready to start another cycle of life from the egg stage.

The silkworm has a spinning apparatus which has been imitated by man in the manufacture of rayon, nylon, and other synthetic filaments. Four glands, symmetrically located on each side of the silkworm near the head, secrete two kinds of silk fluids. The fluid from the two larger glands flows toward the head of the worm and converges at one opening, which is the worm's spinneret. As this fluid is extruded, it is covered by the other fluid coming from the smaller glands. As soon as this combination of silk fluids passes through the spinneret, it is coagulated to form a double filament known as a bave. Each single filament is called a brin. Each brin consists of a central portion, which is the actual fibrous part of silk, covered with another kind of secretion. The fibrous part comes from the larger glands and is known as fibroin. The other secretion comes from the smaller glands and is known as sericin. The sericin is a gumlike substance which cements the two brins of the double filament. We shall find that fibroin and sericin are both protein substances but with radically different physical and chemical properties. After the extruded filaments are coagulated, the worm stretches them and arranges them in a definite order. This is the same principle used in the manufacture of rayon, and we shall find that nylon is similarly made. The great difference is in the speed of extrusion. The silkworm requires about 4 days to spin the 4000 yd of filament that makes up its cocoon, whereas the modern man-made spinning machine will turn out that much filament in a few minutes.

In the normal course of events the silk moth will cut its way through the cocoon, but of course this would ruin the cocoon for the purpose of reeling off the long filaments. Therefore the grub in the cocoon is killed. This is usually done by steaming, after which the cocoons may be stored until they are shipped to a filature, where reeling is done. The outside of silk cocoons, which is the part first spun, consists of a loose, entangled mass of filaments known as floss. However, as the spinning progresses the cocoon becomes denser and more uniform. It is the inner portion which is unwound, reeled, and used for making high-grade silk. The amount varies from 400 to 900 yd.

SILK REELING

Reeling is the operation by which the double silk filament is unwound from the cocoon, two or more filaments being combined to make a raw silk thread. There is some confusion about the terms that designate operations and products used for getting silk ready to knit or weave, so that we shall stress the following definitions. The operation of silk reeling, which is done in a filature, has just been defined. The product of reeling is a raw silk thread (not a yarn). *Silk throwing* is the operation by which two or more raw silk threads are twisted together to make a yarn of some desired size. Both these operations involve the extremely long filaments obtained from silk cocoons. The term spinning refers to the use of short fibers of waste silk which are spun like cotton fibers. The product of this operation is a spun silk yarn. The student must differentiate between the two kinds of silk yarns and silk thread, remembering that this use of the word thread does not refer to sewing silk.

When silk is to be reeled the cocoons are softened in hot water to loosen the floss and permit it to be removed. The hot water also softens and even dissolves some of the silk gum, thus permitting the filaments to be unwound easily. The free ends from five to eight cocoons are joined together to make one thread of reeled silk, which is known as grege, and the grege is then wound on a swift. Considerable expertness is required of the reeler because the filaments of a cocoon are not uniform in diameter. Those on the outer portions are much thicker than those on the inner part of the cocoon (the last part spun by the worm). It is seen that, if a silk thread is to be smooth and uniform, the reeler must periodically start a filament from a new cocoon to avoid thick and thin sections of the grege. The number of cocoon filaments to be reeled together depends on the size of thread desired. For example, in the hosiery trade the standard raw silk thread is 14 denier.

SILK THROWING

Reeled silk is not suitable for knitting or weaving. It must be thrown or doubled, and the job of the throwster is to lay the proper number of reeled threads together and give them a twist to yield a yarn suitable for weaving or knitting. There are several types of thrown silk yarns, which differ in the number of reeled threads twisted together and in the amount of twist given them.

Tram silk, a yarn used in the hosiery trade, is made by twisting 2, 3, or more threads together with a small amount of twist (from 3 to 6 turns per inch). This will make a full, flat yarn with good covering power and hence is suitable for filling yarns in weaving. These yarns are designated as 2-thread tram, 3-thread tram, etc.

Crepe yarns have much more twist in them. For example, the Federal Trade Commission in 1941 set the minimal number of turns per inch for the hosiery industry at 100 turns for a 2-thread crepe yarn, 80 turns for 3-thread, 60 turns for 4-thread, etc. This number is the total for the twist given in both reeling and throwing.

Organzine is a yarn made by twisting in two stages. For example, the reeling twist may be 16 to 20 turns to the left, then 2 or 3 of these threads are doubled with 12 to 14 turns per inch to the right. These yarns are known as 2-thread or 2-fold organzine. They are used for warp yarns in weaving.

Georgette yarns are composed of 2 or 3 reeled threads having almost no twist. These singles are folded with 70 to 75 twists. They are used for filling yarns.

Sewing silk is made in 2- or 3-ply type containing 10 to 50 raw silk threads of 14 denier size.

PHYSICAL PROPERTIES OF SILK

Silk is extruded by the silkworm in the form of a double filament, two fibrets cemented together by a glue or gum. The color varies from a gray to a canary yellow, and most of the color is in the gum, because silk is always much whiter after it has been degummed. The gum on silk gives it a stiff, harsh feel, with a very dull, uninteresting appearance, but after the gum has been removed the silk is very soft and lustrous.

Silk is of course the longest natural textile fiber, as the unbroken filament from one cocoon may be 1000 yd long. The diameter varies in each cocoon, the filament spun first (the outside layers) being about 0.013 mm and that in the inside of the cocoon about 0.008 mm. After the gum is boiled off, the diameter is much smaller. If we express the size of silk in terms of denier, we find that raw silk (in the gum) runs from 1.8 to 3.0 denier, but after degumming the denier of the silk filament is about 1.3.

Microscopical examination of silk shows it to be an almost structureless solid fiber without cells or capillary canals.

The specific gravity of silk is higher than that of most of the textile fibers. For raw silk it will average 1.4 and for boiled-off silk 1.25. Silk is noted for its strength, but this has not only been equaled but even surpassed by nylon and the new high-tenacity rayons. The tenacity of raw silk (in the gum) is 4.6 gm/denier, but after degumming it drops to 3.3 gm/denier, so that in ordinary textile uses we must consider the tenacity of silk to be about 3.5 gm/denier. This must be compared with cotton (4.0), high-tenacity viscose (4.0), saponified acetate rayon (6.0), and high-tenacity nylon (6.5). Silk loses about 15% of its strength when wet.

All textile fibers must withstand a certain amount of stretch or elongation before they break. This property is definitely connected with flexibility and resistance to sudden impacts. In this property, silk does not compare very well with other textile fibers. Silk can be stretched from 10 to 25% before it breaks. This must be compared with 15 to 20% for ordinary viscose, 25 to 30% for ordinary acetate, and 45 to 50% for high impact acetate rayon.

We can look at the elastic property of a fiber in two ways, the real elasticity as measured by its recovery after stretching, and the tension required to stretch it a definite amount. The recovery, after stretching, of silk is considered to be quite good, and yet it is only one-half to three-fourths as much as that of nylon. Silk has a high inertia to be overcome in order to stretch it, an inertia almost as high as that of ramie. The fibers listed require the following amounts of grams tension per denier to stretch them 1% at 65% R.H.: nylon, 0.10; wool, 0.32; acetate rayon, 0.4; silk, 0.75; and ramie, 0.90.

The luster of silk is one of its most desirable properties. Raw silk has very little luster, but after the gum is removed we find the silk with the luster and softness usually associated with it in our minds. This luster is decreased during some dyeing and mordanting operations, but it can be brought back by certain lustering treatments. Two such treatments are commonly used. If the silk is in skein form it may be twisted tightly and steamed, or it may be steeped in acetic acid, squeezed out, and dried without rinsing.

Silk is a very poor conductor of electricity, and for this reason it has been widely used for wrapping wires in electrical equipment. On the other hand, it is quite easily electrified by rubbing. Silk thus presents a problem in some of the manufacturing operations, because it is hard to handle and tends to stick to any metal it touches. This can be avoided by the proper control of humidity.

In hygroscopic properties silk is about midway between cotton and wool, and it is bought and sold on a 11% regain basis. After it is degummed it is less hygroscopic, with a regain of 9.25%.

A special property of silk, which is peculiar to it but not inherent, is scroop. Scroop gives to silk the characteristic rustling or crunching sound and feel when it is squeezed. Silk can be scrooped by dipping it in dilute acetic or tartaric acid and then drying without rinsing.

THE PROTEINS OF SILK

Silk is composed of two similar, but yet entirely different, proteins. The protein of the real fiber is known as fibroin and makes up almost three-fourths of the composition of raw silk. It is insoluble in hot or cold water, hot soap solution, or dilute NH_4OH, and it is not rapidly attacked by 1% NaOH or dilute HCl. It is easily soluble in cold concentrated HCl or other mineral acids, in hot NaOH, and in alkaline solutions of the hydroxides of nickel and copper. Silk is a much simpler protein than wool. When hydrolyzed, it yields eleven amino acids (page 46), of which glycine and alanine make up about 60%. Note that the disulfide amino acid cystine is not found in silk hydrolysate, and therefore silk does not contain any sulfur. Because of this, silk will differ from wool in all reactions or treatments that involve sulfur.

The protein of silk gum or silk glue is known as sericin, which constitutes approximately one-fourth of the weight of raw silk. It is a yellowish, harsh, dull solid which serves as a protective and agglutinizing substance. Its harsh feel and lusterless appearance make it undesirable in finished silk goods, but it serves as such a good protective agent for the fibroin that it is not usually removed until all the mechanical operations have been completed. Sericin is fairly soluble in hot water, and Mosher[1] states that it is completely soluble in alkaline solutions with a *p*H above 9.5, or in acid solutions with a *p*H lower than 2.5. It is therefore soluble in hot soap solutions or weak alkalies or acids, and such conditions are used for its removal from silk goods.

Degumming Silk

Degumming or boiling-off is a commercial process for the removal of silk gum, sericin, from the true fiber, fibroin, and it is done to develop the luster and softness usually found in silk. A good boiling-off must remove not only the silk gum but also the natural fats and oils left by the silkworm and the fats and oils introduced by the throwster when he soaks the silk before the operation of throwing. For the purpose of distinguishing different batches or qualities, the throwster often tints the silk with dyes. These colors, together with natural pigments, must also be removed by the process of boiling-off. When the worker is deciding on the type of degumming agent to be used, he must consider the removal of all these substances. At the same time he must bear in mind the importance of preserving the tensile strength of the silk as well as maintaining the maximum elasticity and luster.

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[1] *Am. Silk J.* **49**, 53 (1930).

There are three main ways in which silk can be degummed: (*a*) in alkaline baths, (*b*) in acid baths, and (*c*) by means of enzymes. Of these three, the first is by far the most important.

DEGUMMING SILK IN ALKALINE BATHS

Of the alkalies available for degumming silk, soap is the most important and the most used. It incorporates most of the factors desired in a boiling-off bath and has very few disadvantages. The raw silk is heated with a 1–2% solution of soap in such a volume that the weight of soap used is equal to about 15% of the weight of silk being treated. However, certain important factors must be considered.

THE *p*H FACTOR

One of the most important factors in boiling-off silk in alkaline baths is the *p*H of the bath. It has been found that the optimum *p*H of a degumming bath is between 10 and 10.5. Below this value the reaction is too slow, and when using solutions having a higher *p*H there is always danger of the silk's losing in tensile strength and coming out harsh. In any processing of silk, it must be remembered that silk is much more sensitive to alkalies than to acids. This is illustrated by the fact that, in a 10-hour treatment of silk with 1 *N* NaOH, 45% of the fibroin is hydrolyzed to amino acids, but with 3 *N* HCl under the same conditions, only 1.5% of the silk is hydrolyzed. This shows that there is little to be feared from the processing of silk in acid baths, for the usual concentration of acid is not great enough to be dangerous. On the other hand, processing in alkaline media must be controlled very carefully. The boiling-off operation is such a process, and the *p*H of the degumming bath should be controlled. If a degumming bath has a *p*H which is too low, then some alkali such as Na_2CO_3 or NaOH may be added to it until the *p*H reaches the desired value.

When soap alone is used, a concentration of 0.053 *N* (which is approximately 15 gm/l) is found to be the most efficient, and this efficiency decreases with soap solutions either weaker or stronger than this. When speaking of the efficiency of a degumming operation, the term degumming coefficient is used. This expresses numerically the proportion of the total sericin removed in a given length of time. This number varies with the concentration of soap solution and reaches its highest value when this is 0.053 *N*.

The soap baths in which silk has been degummed (the boiled-off liquors) find use in the dyeing of silk with acid dyes. These liquors form emulsions with acid solutions (the dye baths) and assist greatly with the penetration of the dyestuff, yielding a more uniform product with a softer feel and more body. But here again *p*H is important, for at a *p*H of 4 these emulsions break, and the fatty material is precipitated and deposited on the goods. This of course is entirely undesirable, but it can be easily prevented by adjusting the acidity of the dye bath to keep the *p*H away from 4. After dyeing, if it is desired to recover the soap and organic material from the dye bath, the *p*H can be brought to a value of 4, at which point the emulsion will break and the fatty material can be skimmed off.

THE TIME FACTOR

The time required for degumming naturally varies with the nature of the raw silk or the type of goods being handled. It will also depend on the temperature. In practice, the time usually runs from 1 to 2 hours.

THE TEMPERATURE FACTOR

Sericin is only slightly soluble below 80° C, but its solubility increases rapidly above this temperature, and most of the degumming takes place between 95 and 100° C. To express this temperature factor more exactly, it has been found that, when using a 0.03 *N* soap solution at 82° C, the degumming coefficient is only 33, but at 95° C it is about 95. It would be reasonable to assume that, if we increase the alkalinity, the time required would be shortened. Studies have been made in which these first three factors, time, temperature, and alkalinity, have been varied. The conclusion reached was that, as far as quality of the product is concerned, there is nothing to be gained by lowering the temperature and lengthening the time or by increasing the alkalinity and shortening the time.

THE SOAP FACTOR

In practice, olive oil soap is usually used for degumming silk. In general, a low-titer soap is desired because it dissolves more readily than other soaps and for this reason can be removed more easily when rinsed.

Additions of various compounds to the soap bath have been recommended. For example, the addition of 1% Na_2CO_3 (based on the weight of silk) has been found to assist in emulsifying the lubricants and oils added by the throwster. Sodium silicate is sometimes added to the extent of about 4%. Its chief contribution is that it helps to maintain a constant *p*H in the bath. This is a real advantage, for the *p*H of the bath will not stay constant unless some reagent of this sort is used. We know that when soap is dissolved in water it hydrolyzes, forming a certain amount of free base and free fatty acid. We have noted before that silk is much more sensitive to alkali than to acid, and for this reason we are not surprised that, when silk has a chance to react with either the free alkali or the free acid in a soap bath, it selects the alkali and combines with it. This removal of free base causes the *p*H of the bath to decrease (it becomes less alkaline). Since sericin and fibroin are so similar we should expect both of them to react with the free base, but the facts are that sericin is so much more reactive than fibroin that the fibroin has little chance, and hence it is sericin that is removed by degumming baths containing soap. More than one batch of silk may be boiled off in the same bath, provided that the lowered *p*H is brought back to its optimum value by the addition of alkali of some sort.

When sericin combines with free base (from soap hydrolysis) it may remain practically unchanged, but if the *p*H is too high or the time too long some of it will be changed (degraded) either by direct hydrolysis or by a general depolymerization reaction. The extent of this degradation is expressed numerically by the binding weight of the sericin. By binding weight is meant the grams of sericin combined with one equivalent weight of alkali in the silk gum solution. The greater the extent of degradation, the less sericin will be combined with alkali, so that the numerical value of the binding weight decreases as degradation of the sericin increases. It will vary between about 2000, when there is practically no degradation, to about 140, when degradation is almost complete. As a general rule, the binding weight decreases as the *p*H of the boiling-off bath goes up, and yet it is influenced more by the ratio between sericin and alkali initially present in the bath.

After a thorough rinsing of silk that has been degummed in a hot soap bath, it is found that a small amount of soap (about 1% of the weight of silk) is retained by the silk. It is not known whether it is held in some physical way or by a chemical combination, but it has its effect on the finished product. This effect is to give the silk a softer feel and particularly a certain amount of body or firmness that is lacking in silk degummed by other methods.

The use of the newer soaplike products, such as sulfonated fatty esters and the fatty alcohol sulfate (Dreft), has not been studied sufficiently to conclude much about their advantages or disadvantages for boiling-off silk.

Other alkaline substances used for degumming silk are the boil-off oils. These consist of sulfonated oils (usually made from castor oil or oleic acid), which are good penetrating agents, mixed with alkali of some sort. These substances depend on the alkali for their degumming action, but the action of the alkali is modified by the presence of the sulfonated oil. The oil decreases the harsh action of the alkali, assists in the removal of natural fats and waxes from the silk, and provides fatty matter, a certain amount of which may be absorbed by the silk and will give more body to it. The use of free alkalies, such as Na_2CO_3, NaOH, and Na_3PO_4, by themselves is not desirable for several reasons. It is difficult to control the *p*H of the degumming bath, and the free alkalies will not remove natural fats and waxes as efficiently as soap will. They tend to attack the fiber and are likely to decrease the luster of the boiled-off silk. These alkalies provide no fatty matter, which is essential for giving body to the silk, and hence they tend to leave the goods limp.

DEGUMMING SILK IN ACID BATHS

Sericin can also be removed from raw silk by an acid treatment, but this method is used very little, for such a treatment fails to remove natural fats and waxes found in silk, which are undesirable when later stages of finishing are reached. The best acid bath to use is one in which the *p*H ranges from 1.75 to 2.75. An acid degumming bath might be employed when thrown silk is woven with wool. The wool might be seriously shrunk if the cloth were degummed with hot soap solution, and in such instances an acid treatment followed by a light soaping would be effective.

DEGUMMING SILK WITH ENZYMES

As sericin is a protein substance, it should be destroyed by a proteolytic (protein-splitting) enzyme. But fibroin is also a protein, and if silk is to be degummed with enzymes the enzymes must act specifically on sericin, or must act upon it so much faster than on fibroin that the fibroin is not harmed during the operation. Most important among the enzymes that have been recommended are:

Pepsin, an enzyme in gastric juice.

Trypsin, an enzyme in pancreatic juice.

Yeast.

Papain, a vegetable enzyme found in the fruit of the papaw, or South American melon tree. It is usually activated with HCN or $Na_2S_2O_3$.

The behavior of various enzymes is governed by the *p*H of the medium in which they act; e.g., pepsin acts in a fairly strong acid medium, but trypsin shows no activity except in basic media.

There are three kinds of degummed silk, based on the extent of boiling-off. If raw silk is simply steeped in hot water it will lose about 3 to 5% of its weight. The resulting product is known as ecru silk. It is considered by some people not to have been boiled off at all. Ecru silk is used for warps.

If raw silk is steeped in soap solution at about 60° C for some hours, it loses about half the gum and is known as soupled silk, and the treatment is called soupling. Soupled silk has lost enough of the gum to be soft and lustrous, but retains enough to give strength to the fibroin. The gum may be fairly well set or fixed by a treatment with cream of tartar. Soupled silk may be used for either warp or filling.

Cuit or boiled-off silk is raw silk that has been boiled with soap solution long enough to remove all the gum. It has the maximum softness and luster, but is weaker than the others. It is used for filling.

CHEMICAL PROPERTIES

As silk is an animal fiber, it will have the composition of a protein and therefore should have properties quite like those of wool. The one big difference between the two is that silk contains no sulfur and so will not react like wool in any way that involves sulfur or cystine or cystine linkages.

Reaction with Acids

Concentrated mineral acids will dissolve silk very easily and much faster than wool. Concentrated HCl dissolves silk in two or three minutes; wild silk, however, is much more resistant. It has been found that HCl of 29° Tw (sp gr = 1.145), which is a 28.6% solution, has a peculiar effect on silk. If silk is immersed in such a solution at room temperature for one to two minutes, the silk contracts about 30%, but there appears to be no degradation or loss in strength if the silk is rinsed immediately. (Solutions weaker than this cause no shrinkage, and solutions stronger than 29.5% destroy silk completely.) This specific reaction has been used for the production of crepon effects on silk fabrics. The cloth is printed with a wax that will resist the action of HCl, and then the fabric is immersed in the acid solution one to two minutes. The unwaxed areas will contract and yield the desired effect.

Dilute mineral acids are absorbed by silk but are not held as strongly as by wool; that is, they can be rinsed off more easily. Too long contact with any dilute mineral acid decreases the luster of silk. Sulfurous acid (SO_2) does not harm silk unless the reaction is prolonged. It will destroy the yellow color and is therefore used as a bleaching agent for silk. Organic acids do not harm silk, and we have already learned that acetic and tartaric acids are commonly used for lustering and scrooping silk. Tannic acid is absorbed by silk in quite large amounts, and one of the methods for weighting silk is based on this fact. Weighting will be discussed later in this chapter.

Action of Alkalies

Silk is not so sensitive as wool to caustic (hydroxide) alkalies. This is probably because silk has no cystine linkages to be damaged by the action of caustic alkalies. This fact does not mean that silk cannot be damaged by caustic alkalies, because silk is a protein and therefore will be hydrolyzed by alkalies if the concentration and temperature are high enough. A boiling 5% solution of NaOH will dissolve silk completely. However, much stronger solutions of NaOH at 0° C will not harm silk. Solutions of mercerizing strength (which will shrink cotton yarns 25%) are examples of this. If a cloth woven from silk and cotton yarns is passed through such a solution of NaOH, the cotton yarns will shrink, the silk will be unchanged, and the result is a crepe effect. Carbonated alkalies are not considered to be harmful to silk, and yet if the temperature is too high a certain amount of harshness and decreased luster may result. This factor is important because it is connected with the degumming and subsequent washing of silk. Any soap used for such a purpose must be free from any alkalinity except that which is due to the soap itself. Otherwise, the results will not be satisfactory.

The Action of Oxidizing Agents

All oxidizing agents will degrade silk just as they do wool, shortening the chain length, reducing the strength, and, especially, making the silk harsh. Hypochlorites must be mentioned specifically. When hypochlorites react with substances, the reaction may be an oxidation or chlorination, depending on the *p*H of the reaction mixture. If silk is subjected to such a reagent, both reactions take place, and the silk is yellowed and weakened. Therefore, hypochlorites cannot be used for bleaching silk. However, hydrogen peroxide does not harm silk unless the *p*H is too high. We can take advantage of this fact and use peroxides (in combination with sulfur dioxide) for bleaching silk.

THE WEIGHTING OF SILK

When raw silk is boiled off it loses almost one-fourth of its weight. The practice of weighting silk was probably started as a means for replacing this weight in order to save money. It was also discovered that a small amount of weighting was desirable. On the other hand, unscrupulous dyers and finishers took advantage of the situation and began to increase the weighting until they were turning out silks that were only one-half or even one-third real silk, and the rest of the material was weighting. Silk can be weighted up to 400%, but excessive weighting is quite undesirable, especially if the silk is stored or subjected to the action of perspiration. It tends to weaken, crack, and become stained.

In 1938 certain Federal Trade Commission rulings were adopted and incorporated within the Trade Practice Rules for the Silk Industry. Among other things, these rules cover the labeling of silk. The word silk, pure silk, or pure dye silk may not be used in labeling or advertising if the goods contain other fibers or any mineral weighting substances whatsoever, except such weight as may have been added during dyeing and finishing, and this added weight must not exceed 10% of the finished product, except for black silk, in which it may not exceed 15% of the finished product. If silk goods are intentionally weighted above these amounts, the fact must be shown on the label. However, a 5% tolerance is permitted because of the difficulty of reproducing goods containing the same amount of weighting. The amount of weighting may be stated on a label in any one of three ways: (*a*) as a simple percentage, e.g., "Silk weighted 30%"; (*b*) as a maximum, e.g., "Not over 50% weighting"; or (*c*) as a range, e.g., "Silk weighted from 25% to 40%."

The Silk Association has set up some maximum limits for weighting which the members are expected to observe. For example, the maximum weighting of satins is set at 50%, crepe de chine and canton crepe at 45%, georgette at 30%, and chiffon at 10%. All commercial silk fabrics available to consumers are weighted a small amount. Pure dye silk is a term applied to either white or dyed silk that has been weighted 10% or less. It has nothing to do with the color of the silk or any dyes that have been used. Additional weight can be given silk in various ways, but they can be divided into two general methods, (*a*) weighting for blacks and (*b*) weighting for white fabrics and for colored goods other than black. The second method is the so-called tin weighting of silk.

WEIGHTING FOR BLACKS

When silk is to be dyed black or some dark color, it makes little difference whether the weighting substances are colored or not, and in fact the color of the weighting sometimes gives a definite and desirable tone to the finished material. The weighting applied to silk which is to be dyed black is a combination of tannic acid and iron treatments. Allowing for minor modifications, the weighting is carried out as follows:

Either raw silk or degummed silk is steeped for several hours in tannic acid solutions at 40 to 45° C. For this purpose a solution of chestnut extract (sp gr = 1.05 to 1.07) is used. The silk will absorb some tannic acid which is fixed by the next treatment. After the silk is squeezed, it is passed to a cold bath of ferrous iron solution. This results in the formation of an insoluble tannate of iron which is deposited on the goods. Iron compounds suitable for such use are pyrolignite of iron (crude ferrous acetate) or copperas (ferrous sulfate) in solutions with a specific gravity of 1.06 to 1.07. After about an hour in the iron bath the silk is squeezed out and exposed to the air to partially oxidize the iron to ferric iron, and it is then washed. The goods will now have increased about 20 to 25% in weight and are ready to be put through the same operations again. Each time this is repeated the weight will be increased until the desired total weight has been obtained. The same baths may be used over and over by adding a little fresh chemical each time. At the end of the weighting, the goods are sometimes given a treatment with potassium ferrocyanide. This reacts with an excess iron to form the insoluble Prussian blue which not only adds more weight but also gives a bluish tone to the material. The silk is now ready to be dyed with some mordant dyestuff such as logwood.

THE TIN WEIGHTING OF SILK

All silk which is to be left undyed or dyed in light colors is weighted by the tin method. There are eight steps in this method, which we shall simply itemize first and then discuss in more detail.

1. The silk is soaked in stannic chloride, $SnCl_4$.
2. It is washed thoroughly.
3. It is steeped in disodium phosphate.
4. It is again washed thoroughly.
5. The first four steps are repeated until sufficient weight has been added.
6. The silk is then steeped in aluminum sulfate, $Al_2(SO_4)_3$.
7. It is steeped in sodium silicate.
8. It is washed and dried.

It may seem odd that we include three steps that are simply washing, but we shall find that two of them are among the series of chemical reactions associated with the weighting of silk. Step 8 is a true washing or rinsing step, but Steps 2 and 4 are hydrolysis reactions in which water takes part. We shall now discuss these steps in detail.

1. In this step, silk is steeped in $SnCl_4$ (sp gr = 1.276) at room temperature for 1 to 1½ hours. Chinn and Phelps[2] found this to be the best concentration of $SnCl_4$ to use so that the silk will retain the maximum added weight, about 10.6% of the original weight. It is thought that an addition product between silk and $SnCl_4$ is formed during this treatment. This product may have a composition such as $Sn(silk)_4Cl_4$. Richter and Muller[3] showed that such a compound is formed when glycine is treated with $SnCl_4$. Glycine is a simple amino acid that is an important component of the hydrolysate of silk fibroin, and because of the analogy with silk it is possible that such an addition compound is formed. On the other hand, it may be that silk simply absorbs stannic chloride as it does salts of aluminum and iron. At any rate, whether the first step is simple physical absorption or chemical addition, the second step is one of hydrolysis.

2. The second step is listed as washing, but it is more than that. After being steeped in $SnCl_4$, the silk is squeezed or hydroextracted in order to remove excess liquid, but this leaves two possibilities. $SnCl_4$ is either chemically combined with the silk or is simply absorbed by the silk. In either event rinsing with water brings about hydrolysis of the material, with the result that metastannic acid, H_2SnO_3 (hydrated stannic oxide, SnO_2H_2O) is precipitated on the fibers.

$$\mathrm{Sn(silk)_4Cl_4 + 3HOH \longrightarrow H_2SnO_3 + 4HCl + 4silk}$$

$$\mathrm{SnCl_4 + 3HOH \longrightarrow H_2SnO_3 + 4HCl}$$

Metastannic acid is insoluble in water and therefore is retained by the silk and adds weight to it.

3. In this step, silk coated with metastannic acid is treated with disodium phosphate. This requires only a dilute solution of Na_2HPO_4 (sp gr = 1.05) at 60° to 70° C. Solutions of Na_2HPO_4 are alkaline because of hydrolysis, and therefore the following reaction will take place:

$$\mathrm{H_2SnO_3 + Na_2HPO_4 \rightleftarrows Na_2SnO_3 + H_3PO_4}$$

and the H_3PO_4 is neutralized by the alkalinity of the bath. Then

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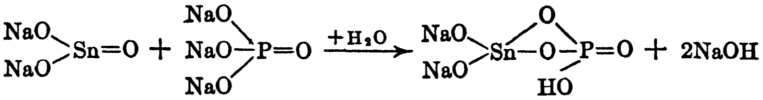
[2] *Ind. Eng. Chem.*, **27**, 209 (1935).

[3] *J. Soc. Chem. Ind.*, **33**, 689 (1914).

Na_2SnO_3 reacts with Na_2HPO_4 to form $Sn(ONa)_2HPO_4$. The material is hydroextracted to remove excess phosphate and is then ready for the next step.



4. This washing is another step in which water reacts chemically. The complex sodium-stannic phosphate is a salt of a weak acid and will therefore hydrolyze to form the corresponding acid, which is insoluble in water.

$$Sn(ONa)_2HPO_4 + 2HOH \longrightarrow Sn(OH)_2HPO_4 + 2NaOH$$

5. The tin phosphate compound which has been deposited on the silk is very heavy, with a molecular weight of 249. The specific gravity of this compound is not known, but it is probably about 4. Although only a small amount of this compound may have been deposited on the silk, the weight of the silk will have been considerably increased. If a greater increase in weight is desired, the silk is put through the same four operations until the weight has increased sufficiently.

6. The goods are then immersed in a bath of aluminum sulfate (sp gr = 1.03) at 40 to 50° C for 1 to 1½ hours. There is some difference of opinion about what is accomplished by this treatment. Presumably any alkalinity left in the goods will react with aluminum sulfate to form some aluminum hydroxide which will be deposited on the goods and give a little additional weight.

7. The next step is immersion of the weighted goods in a solution of sodium silicate (sp gr = 1.04) at about 50° C. This may form some sort of a tin-silico-phosphate, the composition of which has not been determined.

Various modifications of the above general method have been used. For example, it is claimed that if the stannic chloride is dissolved in a strong solution of sodium chloride a lower concentration of tin is required, a more rapid exhaustion of the bath is obtained, and less tin is lost in washing. Carbonates have been added to the $SnCl_4$ bath. Those such as calcium, barium, and magnesium would react with the HCl of the bath to form soluble chlorides and then when treated with sodium phosphate would yield insoluble phosphates. Numerous patents have been taken out to protect the use of the addition to, and the substitution in, the baths of all sorts of compounds, but the general method still remains about the same.

It is seen that all the weighting substances applied to silk by the tin method are colorless compounds, and therefore the weight of the silk may be increased without changing its color. For this reason the tin weighting method is suitable for use with white or light colored silk fabrics or threads.

ANALYSIS OF WEIGHTED SILKS

The determination of the amount of weighting on silk is important because of the high cost of silk. Added weight that may be given cotton or rayon is of very little economic importance because the cost of the fibers being weighted is low.

If one is interested only in a qualititative examination of a silk fabric to determine whether or not it has been weighted, one may depend on the feel of the cloth and the way it burns. A weighted silk feels stiffer, more compact, less flexible, and scroopier than unweighted silk. When a weighted silk is burned, an abnormally large amount of ash is left. If it is weighted heavily enough, the ash will have the same shape and form as the original cloth, may even be picked up and handled, and will show the same appearance of warp and filling yarns.

The percentage of the ash is quite a good quantitative measure of weighting. This is probably the quickest and simplest method for the quantitative determination of weighting if the weighting has been applied by the tin method. For a detailed description of the best method for the determination of weighting see Mease.[4]

There are two methods for expressing the amount of weighting in silk. One way is to express the amount of weighting as a percentage of the weighted silk. That is, if a 0.5-gm sample of weighted silk is found to contain 0.3 gm weighting, the percentage weighting will be $(0.3 \div 0.5) \times 100 = 60\%$. This means that 60% of the weighted silk is material that has been added intentionally, and the other 40% is real silk fibroin.

The other method is to express the weighting on the basis of ounces per pound of raw silk, with the assumption that 1 lb of raw silk contains 12.4 oz of pure silk fiber (boiled off). That is, how many ounces of the weighted silk have been produced from 1 lb of raw silk? Of course when the raw silk is boiled off, it will lose weight, and this weight may be restored by weighting, up to and beyond the original weight. If 1 lb (16 oz) of raw silk is boiled off and then weighted until it weighs 31 oz, more than 15 oz of weighting must be added. A tolerance of 2 oz is allowed, and such a silk would be designated as a 30/32 oz silk. Let us take the same sample, 0.5 gm of which contained 0.3 gm of weighting material, and calculate how the silk would be described by this system. We want to find out how many ounces of this silk could be made from 16 oz of raw silk, which contains 12.4 oz of real silk fibroin. We shall first calculate the percentage of weighting based on the real silk. We find that there is 0.3 gm weighting for 0.2 gm real silk, which is 150% weighting based on the real silk. This percentage of 12.4 oz is 1.5 times 12.4, or 18.6 oz. This means that, for every 12.4 oz of real silk fibroin, 18.6 oz of weighting have been added. The total is 31 oz. That is, 31 oz of weighted silk have been made from 16 oz of raw silk, and this silk would be known as a 30/32 oz silk.

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[4] "The Analysis of Weighted Silk," *J. Research Natl. Bur. Standards*, **9**, 669 (1932).

THE WILD SILKS

There are several types of caterpillars other than Bombyx which spin cocoons suitable for silk manufacture. As these are not cultivated or domesticated, they are called wild silkworms, and the filaments obtained from their cocoons wild silks. The most important of the wild silks is known as tussah or tussur. It is produced by *Antheraea pernyi*, which is native to China and feeds on the leaves of one general type of oak, *Quercus serrata.* Wild silks of lesser importance are known as eria, mnga, and yamamai.

Tussah cocoons are larger and darker and have thicker filaments than mulberry silk. Under the microscrope the filaments appear almost ribbon-shaped and quite fibrillous. Tussah cocoons have more gum than mulberry cocoons and also contain a complex calcium compound which is hard to remove. This makes it necessary to give the cocoons several boilings and rinsings with soda water and clean water before the silk can be reeled. Reeling is often not even attempted, but the cocoons are picked apart into a silk staple fiber which is spun like cotton. Tussah silk is more resistant than mulberry silk to all chemical reagents.

SPUN SILK

This is often called waste silk because it is silk that cannot be reeled. Two types are well known, schappe silk and bourette silk.

Schappe silk is produced from the outer and inner parts of cocoons and from cocoons that have been pierced by the escaping moth and therefore cannot be reeled. The cocoons are treated with alkaline baths or in alkaline solutions containing enzymes. After washing and drying, the filaments are picked off, combed, and spun like worsted.

During the picking, combing, and spinning of schappe silk, a considerable amount of waste is formed. This is a short-staple silk which is carded and spun like woolen yarn. It is called bourette silk, or silk noils.

Waste silk that eventually becomes spun silk is classified into gum waste and throwsters' waste. Gum waste is an accumulation of all waste obtained before and during reeling. It is subdivided into several types, depending on the method of formation. For example, floss is the tangled mass of filaments on the outside of the cocoons which cannot be reeled without breaking it. As the reeler tries to find the loose end of the cocoon filament preparatory to reeling, a long type of waste known as frison is obtained.

QUESTIONS

1. Tell the life story of the silkworm.
2. How much silk filament is in one cocoon? How is the silk filament made up?
3. What is silk reeling? How is it done? What is silk throwing?
4. What is tram silk? organzine? crepe?
5. Discuss the physical properties of silk.
6. What is the physical and chemical difference between silk fibroin and sericin?
7. How do silk fibroin and sericin react with hot water? with warm NaOH?
8. How is silk degummed by the alkaline bath method? What is the optimum *p*H for the degumming bath? What is the objection to the use of baths with higher or lower *p*H? What kind of soap should be used? At what concentration? How long should it take? What is the best temperature?
9. In what other ways can silk be degummed?
10. How do silk and wool differ chemically?
11. How does silk behave when immersed in concentrated HCl?
12. Compare silk and wool in their sensitivity to caustic alkalies and to mineral acids.

13. Is it permissible for silk goods to be labeled pure dye silk if they are weighted to the extent of about 8%?

14. Give three labels that might be put on a silk that contains 30% weighting?

15. If a piece of dress goods is made with 80% silk and 20% rayon, may it be labeled and advertised as silk?

16. Outline the steps used in the tin weighting of silk. About how much additional weight does silk acquire when put through these steps once? About how much weighting would a "heavily weighted" silk contain?

17. If silk is to be dyed black or some dark color, in what other way may it be weighted?

18. Tell what is meant by the following terms:

wild silk
bave
grege
schappe
gum waste
spun silk
brin
boiling off
bourette
frison

11 · Nylon

When one hears the word nylon the first thought is of hosiery, but many other materials are made from nylon, such as shirts, blouses, slips, lingerie, uniforms, parachute fabric, toothbrush bristles, sheets, ropes, tennis rackets, and screening for windows. Since these materials are varied, it is obvious that there must be many kinds or types of nylon. Then what does the word nylon signify? It is a generic term applied to many products that may be obtained by the polymerization of mixtures of diamines and dicarboxylic acids, these products constituting an entirely new family of organic chemicals. The word has no etymological significance but is merely a new word for a new group of chemical substances. The word was chosen by men in the du Pont organization because it was different, easy to pronounce, and had a pleasant sound.

The du Pont Company has defined nylon as a generic term for any long-chain synthetic polymeric amide that has recurring amide groups as an integral part of the main polymer chain, and that is capable of being formed into a filament in which the structural elements are oriented in the direction of the axis. This definition does not say that nylon must be used for hosiery or fabric manufacture, but intimates that it is a raw material from which many things, such as fibers, bristles, sheets, and other useful products, might be made. All these forms are characterized by extreme toughness, elasticity, and strength. As students of textile chemistry, we are interested in nylon only as a raw material which forms the basis for the fabrication of filaments which can be converted into yarns for knitting and weaving.

When we realize that during part of 1945 and 1946 nylon hose ranked with some of the scarce food essentials in publicity, clamor on the part of the public, and radio comment, we must admit the importance of nylon, and considerable space in this book will be devoted to it. It has been called a supersilk, and when we come to discuss its properties we shall perhaps agree with such a statement. But before studying its manufacture, properties, and uses, it will be interesting to learn something of the history of its development.

HISTORY OF NYLON

Nylon was developed by a group of research organic chemists working in the laboratories of the E. I. du Pont de Nemours Company in Wilmington, Del., under the direction of Dr. Wallace H. Carothers. The entire project is one of the best examples of what may be accomplished by a broad program of research in pure science in the hands of adequately trained men, working with no thought but the contribution they may make to pure science, and sponsored by an understanding organization that permits unhampered and unhurried work. This program was instituted by the du Pont Company in 1928, when they put Dr. Carothers in charge of a small group of men who were to explore both new and old realms in the field of fundamental research. Strange as it may seem, Dr. Carothers was told that he might select any problem he wished. He chose to work in the field of polymerization, where small molecules are made into giant molecules having molecular weights greater than 10,000 or 20,000. As a result of this fundamental research, coupled with great engineering skill and the cooperation of a management with imagination, we have the new wonder substance, nylon.

Nylon is a protein-like substance, that is, a nitrogenous substance composed of long chains, a high polymer. And yet, at first, Carothers was interested in polymers obtained from acetylene derivatives, which resulted in the discovery of Neoprene, a synthetic rubber-like material.

Carothers and his co-workers were also interested in high polymers that could be made from dibasic acids and dihydric alcohols. They caused such compounds to condense with each other and yield huge molecules with molecular weights as high as 5000. As condensation in this instance involves the splitting out of molecules of water (see page 312), it was thought that, if the high polymer were to be heated under high vacuum, which would help get rid of the water, more molecules would condense and a higher polymer would result. To accomplish this, a molecular still was devised in which the polyester was distilled, and further condensation took place to such an extent that the molecular weight went up to about 25,000. These much higher molecular weight polyesters were named superpolyesters.

Not only did these superpolyesters have higher molecular weight, but they had quite different and improved physical properties. Before distillation these esters were opaque, waxy, brittle substances, but after distillation they were semitransparent, tough, and elastic. These superpolyesters could be melted and forced through a small opening (extruded) to yield a wirelike filament. These filaments seemed to promise very little practical use, but in 1930 it was found that they could be drawn out while hot to several times their length. Filaments made in this way were superior to those made by simple extrusion, but much more important was the fact that these new stretched filaments could be drawn out still farther after they were cold. This operation, known as cold drawing, made the filaments more transparent, lustrous, and, still more important, stronger, more flexible, and more elastic.

From this date the point of view of the du Pont research group was changed entirely. It was no longer concerned with problems in pure research, but was definitely pointed toward the perfecting of a synthetic textile fiber. The road was rough. Many, many combinations of compounds which could be condensed to long chains were tried. Some of the resulting filaments were too weak, some too brittle, some too stiff, some melted at too low temperatures, etc. It took five years to find the currently preferred combination, adipic acid and hexamethylene diamine, and in February 1935, polymer 66 and fiber 66 were made. The significance of the 66 is that each molecule of the dibasic acid and the diamine has six carbons. Between this date and the latter part of 1939, many practical problems had to be solved. In the first place, the two chemicals from which nylon is made were more or less laboratory curiosities. They could be made in the laboratory, but such small batches would not make nylon enough for 175,000,000 pairs of nylon stockings (the number made in 1941). All sorts of engineering problems had to be solved. In 1936 a plant was developed for making adipic acid in large amounts, and from this adipic acid making hexamethylene diamine. In 1937 the first experimental stockings were knit from the new yarn; in 1938 a pilot plant was built; during 1939 and part of 1940 more than 150,000 pairs of nylon stockings were being worn by American women in order to test them (these were made of 30, 40, and 70 denier yarns); in May 1940 nylon stockings were made available in all the principal cities of the country, and about 64,000,000 pairs were sold during that year.

MANUFACTURE OF NYLON

Nylon is a thermoplastic polymer which may be made to have quite a wide variation in physical properties, depending on the conditions under which it is produced. Remember that nylon is a generic name and does not necessarily apply to the yarn from which hosiery is made. Variations in the composition of the reaction mixture and in the temperature and time of the reaction will determine the properties of the final product, so that some nylons might be suitable for making textile fibers and others might not be good fiber-forming materials at all. It has been found that nylon can be made from mixtures of about 15 different diamines and 15 different acids. This makes possible about two hundred combinations, and the product of the polymerization of any of these combinations will be a nylon. When first made, nylon is in the form of white flakes, and these flakes are just as much nylon as the yarns in a stocking. If these flakes are manufactured by a certain procedure they may be suitable for making yarns, whereas if they have been made by a different procedure they may be entirely unsuited for making textile fibers but may be perfectly good for manufacture into other useful articles. At this point in our study we are interested in the resin itself, how it is manufactured, and the chemical reactions involved in making it.

It has been said that nylon is a magic material manufactured from coal, air, and water. This has been quite mystifying to the layman because he gets the impression that by some necromancy the scientist has been able to mix these three common substances, go through some hocus-pocus with them, and the result is miles of nylon yarn. Of course this is not true. It is true that in a very, very indirect way adipic acid can be made from coal. Along the way ammonia must be used, and it is produced from the nitrogen of the air and hydrogen, which may be considered as produced from water, although there are other methods for making hydrogen. Actually nylon is made by heating mixtures of adipic acid and hexamethylene diamine, as a result of which linear condensation polymers are formed.

We must pause here to give a few definitions of terms used in connection with the production of superpolyamides. These definitions and many of the statements to be made on the following pages are quoted from some of the basic patents covering nylon granted to Dr. Carothers and assigned to the du Pont Company.[1] The Carothers patents are works of art in that they are written in beautifully clear-cut style, free from ponderous legal verbiage, and replete with specific examples free from evasion. It is regretted that lack of space prevents us from quoting from them at more length.

Condensation is any reaction that occurs with the formation of new bonds between atoms not already joined, and proceeds with the elimination of elements (H_2, N_2, etc.) or simple molecules (H_2O, C_2H_5OH, HCl, etc.).

Condensation polymers are compounds formed by the mutual condensation of a number of (functionally) similar molecules to form a single molecule.

Linear polymers are compounds whose molecules are long chains built up from repeating units. This type of structure may be represented by

$$\cdots\text{—A—A—A—A—A—}\cdots$$

A structural unit of a linear polymer is the unit or fragment —A— which is repeated along the chain.

Linear condensation polymers are linear polymers formed by the reactions of condensation, defined above.

In a general explanation of the making of nylon, Carothers stated in his patent (U.S. 2,130,948), "My fiber-forming polyamides are prepared by heating in substantially equimolecular amounts a diamine and a dicarboxylic acid or an amide-forming derivative of a dibasic carboxylic acid under condensation polymerization conditions, generally 180° to 300° C, in the presence or absence of a diluent, until the product has a sufficiently high molecular weight to exhibit fiber-forming properties. The fiber-forming stage can be tested for by touching the molten polymer with a rod and drawing the rod away; if this stage has been reached, a continuous filament of considerable strength and pliability is readily formed."

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[1] U.S. Patents 2,071,250, 2,071,251, 2,071,253 (1937); 2,130,523 (1938); and 2,130,948 (1938).

If one molecular weight each of adipic acid, ($HOOC—(CH_2)_4—COOH$), and hexamethylene diamine, ($H_2N—(CH_2)_6—NH_2$), are warmed with about 1250 ml of 85% ethyl alcohol, a clear solution should result. That is, any reaction product will be soluble in the alcohol. What reaction product would be expected? We know that the diamine is a base and the adipic acid is an acid, and therefore the product should be a salt, like an ammonium salt. Thus the product of this reaction will be a salt of adipic acid (an adipate), and it will be called hexamethylene-diammonium adipate. When the solution is cooled, a white crystalline solid will separate. This is the salt. It has a melting point of 183 to 184° C and can be recrystallized from 85% alcohol.

What is a salt? In the solid crystalline state it is composed of positive and negative ions arranged in the form of a crystal lattice, and when it is dissolved in water it dissociates into its component ions. Therefore the salt formed by the above reaction may be considered as a mixture of the two ions, the adipate ion $—^{-}OOC—(CH_2)_4—COO^{-}—$, and the hexamethylene-diammonium ion, $^{+}NH_3—(CH_2)_6—NH_3^{+}$. This is really no different from the reaction between acetic acid, CH_3COOH, and ammonia, NH_3, to form ammonium acetate, $CH_3—COONH_4$, the ions of which are acetate, $CH_3—COO^{-}$, and ammonium, NH_4^{+}.

We know that the result of heating ammonium acetate is acetamide, which may be written as:

$$CH_3—COO^{-} + H_2NH_2^{+} + \text{heat} \longrightarrow CH_3—CO—NH_2 + H_2O$$

We see that, according to definition, this is a condensation reaction, because it conforms to the definition previously given. The reaction between adipic acid and hexamethylene diamine is like that of acetic acid with ammonia, and can be shown by the following equation:

$$HOOC—(CH_2)_4—COOH + H_2N—(CH_2)_6—NH_2$$
$$\longrightarrow HOOC—(CH_2)_4—COO—NH_3—(CH_2)_6—NH_2 + HOH$$

The product of this reaction is a salt, like ammonium acetate, which exists as two ions, $HOOC—(CH_2)_4—COO^{-}$ and $^{+}NH_3—(CH_2)_6NH_2$, which will react with each other, when heated, to form a condensation product (see above), as shown below:

$$\mathrm{HOOC—(CH_2)_4—COO^- + {}^+NH_3—(CH_2)_6—NH_2} + \text{heat}$$
$$\longrightarrow \mathrm{HOOC—(CH_2)_4—CO—NH—(CH_2)_6—NH_2 + HOH}$$

Let us simplify this by letting $\mathrm{(CH_2)_4 = R}$ and $\mathrm{(CH_2)_6 = R'}$, and then the condensation product will be

$$\mathrm{HOOC—R—CO—NH—R'—NH_2}$$

It is seen that the left end of this molecule is an acid which can react with more diamine to form a salt and upon heating can split out water to yield an amide as before. Furthermore, the right end is basic and can react with more adipic acid to form a salt which will lose water when heated. These two reactions are shown in the following equation, using R and R′.

$$\mathrm{H_2N—R'—NH_2}$$
$$\mathrm{+ HOOC—R—CO—NH—R'—NH_2 + HOOC—R—COOH} \longrightarrow$$
$$\mathrm{H_2N—R'—NH_3—OOC—R—CO—NH—R'—NH_3—OOC—R—COOH}$$

This compound is like a diammonium salt which will exist as the following ions,

$$\mathrm{H_2N—R'—NH_3^+ + {}^-OOC—R—CO—NH—R'—NH_3^+}$$
$$\mathrm{+ {}^-OOC—R—COOH}$$

and when heated will condense to yield the following condensation product.

$$\mathrm{H_2N—R'—NH—\boxed{\mathrm{CO—R—CO—NH—R'—NH}}—CO—R—COOH}$$

It is evident that a linear condensation polymer is being formed, and that the unit which will be repeated down the chain is $\mathrm{—CO—R—CO—NH—R'—NH—}$ with 14 atoms in the chain. This is the structural unit of nylon 66 polymer, and it is a protein-like unit.

The structural unit of nylon may be varied in length, depending on the length of the groups R and R′. For example, the unit length of the nylon just described is 14, but if sebacic acid, $\mathrm{HOOC—(CH_2)_8—COOH}$, is condensed with pentamethylene diamine, $\mathrm{H_2N—(CH_2)_5—NH_2}$, the structural unit of the resulting polymer will be $\mathrm{—CO—(CH_2)_8—CO—NH—(CH_2)_5—NH—}$, with

17 atoms in the chain. If sebacic acid is condensed with propylene diamine, $H_2N—(CH_2)_3—NH_2$, the structural unit will be $—CO—(CH_2)_8—CO—NH—(CH_2)_3—NH—$, with 15 atoms in the chain. Polyamides with structural units as long as 25 have been made. To make this one, pentamethylene diamine was condensed with hexadecamethylene dicarboxylic acid, $HOOC—(CH_2)_{16}—COOH$. All such polyamides go under the general name nylon, and they are all covered by the Carothers patents. Such condensation reactions might go on indefinitely to form huge molecules with very high molecular weights. This is polymerization, the combination of small molecules to yield very large ones. In this instance, these are condensation polymers, and each time condensation takes place water is formed. This water slows down and will even stop the polymerization, unless it is removed. This was accomplished in the experimental laboratory by means of the molecular still. Therefore by the proper selection of acid and diamine, the control of the temperature and time of heating, and removal of volatile products of the condensations, many kinds of nylon can be made. Some of them are suitable for spinning into textile fibers with the proper strength, flexibility, elasticity, durability, etc., whereas others are entirely unsuitable for making textile fibers because they may have too low a melting point or too high a melting point, or they may be too brittle, inelastic, etc. If the polymerization goes too far, the product has too high a melting point to be worked properly into a textile filament, and the fiber will be too brittle.

Staudinger[2] says that the average number of members in nylon chains runs from 210 to 1600. If this number is lower than about 300, more condensation will take place during spinning due to the heat required for the spinning operation. If the number is higher than 300, the nylon can be spun from single jets of 0.2 to 0.5 mm diameter, but if the product has too high a molecular weight it is degraded during spinning because of the higher temperature required.

In practice the extent of polymerization is controlled to stop it at the proper point by using a small excess (0.1 to 5.0%) of either one of the reactants or by the use of a monofunctional reactant which will break off the ends of some of the reacting molecules. Such added materials are known as stabilizers, and the

[2] C. A., **38**, 4807 (1944).

product obtained is called a stabilized polymer because it will not be further altered at the spinning temperatures required for extrusion.

LARGE-SCALE MANUFACTURE OF NYLON RESIN

Before discussing this subject we must briefly describe the methods by which the immediate raw materials, adipic acid and hexamethylene diamine, are made.

The starting material for the manufacture of adipic acid is benzene, C_6H_6. When benzene is treated with chlorine gas in the presence of an iron catalyst, a liquid, chlorobenzene, C_6H_5Cl, is formed. Phenol is made from chlorobenzene by hydrolyzing it with water at high temperatures (about 425° C) with silica, SiO_2, as a catalyst. In the presence of finely divided nickel, phenol will react with hydrogen gas to form cyclohexanol, $C_6H_{11}OH$. (This is a saturated aliphatic ring alcohol with six carbons in the ring and all valences satisfied.) When cyclohexanol is heated with nitric acid, the ring opens up and the end carbons are oxidized to carboxyl groups, COOH, to yield adipic acid. This sequence of reactions is shown below in a condensed form.

$$C_6H_6 \xrightarrow[Fe]{Cl_2} C_6H_5Cl \xrightarrow[SiO_2]{HOH} C_6H_5OH \xrightarrow[Ni]{H_2} C_6H_{11}OH$$

$$\xrightarrow{HNO_3} HOOC—(CH_2)_4—COOH$$

Adipic acid is a white crystalline solid melting at 153° C. It is very slightly soluble in water, less soluble in ether, but very soluble in alcohol.

Hexamethylene diamine is made from adipic acid by converting it into its diammonium salt and heating this salt to form the diamide of adipic acid, $H_2N—CO—(CH_2)_4—CO—NH_2$. The amide is then treated with hydrogen gas in the presence of nickel. This reduces the two CO groups to CH_2 groups, which makes six of them, and we now have hexamethylene diamine, $H_2N(CH_2)_6NH_2$.

In the large-scale manufacture of nylon, the diamine and the dicarboxylic acid are added to water to form the salt, which then dissolves in the water. This solution is shipped to the spinning mill, where it is heated in large evaporators until a concentrated solution is obtained. The concentrated solution is then transferred to an autoclave, which is provided with a stirring device and heated by circulating dowtherm (a very high-boiling liquid) through the jacket and coils. This is where condensation occurs, the reaction between adipate ions and hexamethylene-diammonium ions, to form long-chain molecules of a polyamide. Since the reaction must be carried out in the absence of oxygen, the autoclave is evacuated and then filled with nitrogen at a pressure of about five atmospheres. The mass is heated for about 4 hours at about 250° C, and during this period nitrogen gas is bubbled through the molten mass. This serves two purposes: (*a*) it makes certain that no oxidation will take place (which would discolor the nylon), and (*b*) it carries out the water formed during the condensation, thus functioning like the molecular still in the laboratory. During this operation, polymerization continues to take place, water is removed, and the polyamide is converted into a superpolyamide with a very high molecular weight. After the polymerization has been carried to the desired extent, the hot mass is ready to be extruded through a slot in the bottom of the autoclave, but it has been found advisable to reduce the pressure first by evacuating, and even to take the pressure down below atmospheric pressure, about 300 mm pressure.

The mass is then allowed to flow out of a slot onto a casting wheel. This wheel revolves slowly, and as the ribbons of molten resin are deposited on it they are sprayed with cold water which hardens them to opaque, milky white, translucent ribbons. The ribbons are picked off the casting wheel and taken to a cutting machine, where they are chipped into a flake form. Nylon yarn is made from these flakes.

PRODUCTION OF NYLON FILAMENT

The conversion of nylon flakes into filaments suitable for twisting into textile yarns consists of two steps, the spinning of an unoriented filament and the stretching of this filament into one that is highly oriented. When we say that something is unoriented, we mean that its constituent parts, or structural units, are arranged in a random, helter-skelter way, with no particular organization. The physical structure of such a substance is said to be amorphous (as distinguished from crystalline). When we say that something is oriented, we mean that its structural units are arranged in some more definite way and that it is well organized. The physical structure of such a substance is said to be crystalline. Common examples of such substances are flour and table salt. Flour is an unoriented, amorphous substance, and salt is an oriented, crystalline solid. When we consider fibers, it is not quite so simple. Fibers, whether natural or synthetic, have a mass structure which can be seen with the naked eye, but they also have what is known as a fine structure, which cannot be seen but can be photographed by X rays. An X-ray picture of an oriented fiber (or filament) will show a predominance of crystallinity, whereas an unoriented fiber will show only small sections of crystalline substance.

There are three general ways in which nylon can be spun into a continuous filament. In the wet process (wet spinning), the polyamide is dissolved in a solvent such as phenol and forced through a small orifice into a liquid (water) which will dissolve the solvent but will not dissolve the polyamide, and therefore it will appear as a long continuous filament. A second method is known as the dry process. When nylon filament is spun by this process, the nylon flakes are dissolved in some solvent, such as formic acid, which can be evaporated, and, when such a solution is forced through an orifice and the solvent evaporated, the result will be a long unoriented filament of the polyamide. The most important of the three methods may be called the melt process.

In this process the molten polyamide is extruded through small orifices into the atmosphere, where it is congealed into a filament. (By a similar process, nylon resin can be converted into rods, bristles, sheets, foils, ribbons, films, etc.) The molten mass may be forced through a single orifice or through a spinneret with many orifices in it. Such a spinneret is a metal disk, about 1.5 in. in diameter, pierced with cone-shaped holes, the tip end of each being a very fine opening, sometimes only about 0.008 in. in diameter. The size of these openings is one of the factors in determining how fine or coarse a filament will be made. As each opening of a spinneret will form one filament, the number of openings will determine the number of filaments in the yarn that will be made. After the filaments leave the spinneret and before they are congealed, they narrow down and become smaller. The size of the thread as well as the size of each individual filament is determined by the amount of polymer extruded per unit of time (grams per minute) as related to the speed with which the congealed yarn is wound up (feet per minute). The orifices in the spinneret are like tiny funnels. The molten polyamide enters the wide end of the funnel and is squeezed out through the small end. The pressure required to accomplish this may be provided by a gas or by a system of pumps which will force the very viscous mass through the spinneret. If gas pressure is used, it must be that of an inert gas, free from oxygen, because oxygen must be excluded from the hot polymer. In actual practice pumps are used, and these pumps must squeeze out all air bubbles and deliver the viscous liquid to the spinneret at a constant rate. Before the material is pushed through the spinneret, it must be filtered. This is done by pumping it through a layer of sand. As the group of filaments emerge from the spinneret and congeal (or freeze), they are picked up on a rapidly revolving drum and are then ready to be cold drawn.

In the large-scale production of filaments, nylon flakes from several autoclave batches are mixed or blended and poured into the hopper of the spinning machine. This insures uniformity in the final nylon yarn. Since the polymer is to be heated above its melting point, and while hot must not come into contact with oxygen, the entire spinning system is flushed out with pure nitrogen, and an atmosphere of nitrogen is maintained until the resin is extruded. The bottom of the hopper is provided with a valve which opens to let the nylon flakes fall onto a hot grid, which melts them, and the molten mass at a temperature of 210 to 290° C is passed to a chamber from which it is pumped through the sand filter to the spinneret. If a multi-filament yarn is being produced, the several separate filaments, after they cool, converge and pass into a conditioner where they are moistened sufficiently to make them stick together and form one single thread.

Very fine filaments can be obtained in this way, some of them as small as 0.2 denier. It would require about ten such filaments to make a thread the size of the cocoon thread spun by the silkworm. The size of nylon yarns depends on two things, the number of individual filaments and the size of each filament. The number of filaments is determined by the number of orifices in the spinneret, and the size of the filaments is ~~determined by the~~ weight of polymer extruded per minute, together with the speed of the rotating take-up drum. These factors are adjusted so that a yarn of specific size may contain the desired number of filaments. For example, two 40 denier yarns are produced commercially, one containing 13 filaments and the other 34 filaments. Each filament of the first yarn is 3 denier, whereas each in the second yarn is a little heavier than 1 denier.

Up to this point no great molecular change has taken place; that is, the chemical structure of the filaments is just about the same as the flakes from which they were made. The only difference is that their physical form has been changed. The arrangement of the long chains of polyamide is still a random one. The filaments are opaque like the flakes; they have poor pliability and are not very strong. However, filaments produced in this way, with very little stress, have the remarkable property of accepting a permanent elongated and oriented form when they are subjected to a drawing operation at ordinary or slightly elevated temperatures. This is the cold drawing operation. The stretching operation produces a profound change in the fine structure of nylon. As stretching begins, the filament separates into two opaque sections joined by a thinner transparent section, and as stretching continues the transparent section grows at the expense of the opaque sections until the latter practically disappear. Filaments can be stretched from two to seven times their original length.

Cold drawing brings about a very desirable molecular change in nylon. This change consists of a gradual rearrangement of the long polyamide chains, from their unoriented, random arrangement to a definitely true fiber-oriented one. The long chains are lined up side by side, parallelized, and brought very close together. This makes it possible for strong intermolecular forces to come into play, so that the elongation is accompanied by a progressive increase in tensile strength until a definite limit is reached beyond which further drawing will break the filament. An increase in tensile strength of 100 to 200% may be obtained in this way. Elongation produced by this cold drawing operation is permanent, so that the yarn will not shrink and regain its original length. The yarn is now strong, more pliable, more flexible, more elastic, and tougher. All these new and desirable properties are obtained by the simple procedure of stretching.

In practice, the cold drawing is accomplished by the use of two rotating drums. That is, the yarn is taken off one drum and wound onto a second one which is rotating much faster, and this means that the yarn will be stretched between drums. For example, the first drum may be rotating at a speed of 300 feet per minute and the second one at a speed of 1530 feet per minute.

Yarn carried by these drums will be subjected to a stretch of about 360%. Finished, stretched nylon yarn may be taken off at a rate as high as 3000 ft per minute.

TYPES OF NYLON YARN

Nylon filaments are uniform, smooth, and cylindrical, and therefore will make a very compact yarn. Filaments can be spun over a wide range of diameters, from 0.00015 to 0.0015 in. The deniers covering this range will vary roughly from 0.1 to 10.0 denier. The du Pont Company is in commercial production of a 15 denier single filament for hosiery (diameter = 0.0017 in.). A monofilament 0.012 in. in diameter is being made for screening. We have learned that the strength of nylon filaments can be improved by cold drawing, as a result of which filaments of different tenacities can be manufactured. At the present time there are two types of nylon yarns offered for sale, a *standard yarn* and a *high-tenacity yarn*. These two types have different strengths and different elongations. The general rule is that the higher the tenacity, the lower the per cent of elongation.

Standard yarns have a tenacity of 4.5 to 5.0 gm/denier (corresponding to about 66,000 to 70,000 psi), and an elongation of 18 to 22% before breaking. A 60 denier yarn would be made by twisting about 20 filaments (each 3 denier), and it would require about 0.6 lb pull to break it. A 40 denier yarn could be broken by a pull of about 0.4 lb.

At the present time five sizes of standard yarns are being sent to the hosiery industry. These sizes and the number of filaments in each are as follows: 15 denier 1 filament, 20 denier 7 filaments, 30 denier 10 filaments, 40 denier 13 filaments, 40 denier 34 filaments, and 60 denier 20 filaments. It is seen that all of these are 3 denier filaments except the 40-34, which is only slightly heavier than a 1 denier filament, and the 15 denier monofilament.

High-tenacity yarns have a tenacity of 6 to 8 gm/denier (corresponding to 88,000 to 114,000 psi) and elongations of 11 to 17%. They are furnished in four different sizes, 70 denier 34 filaments, 100 denier 34 filaments, 150 denier 68 filaments, and 200 denier 34 filaments. The 70 denier yarns are used by the hosiery trade, but the heavier ones are not. The average breaking strength of these high-tenacity yarns ranges from about 1 to 3 lb.

Nylon yarns may also be divided into bright and dull yarns.

When nylon filaments are made by the processes already described in this chapter, they are bright and lustrous. For some purposes this is desirable, but for others it is quite undesirable. However, this objection can be overcome by certain delustering methods. Luster is produced by the reflection of light from a smooth surface, like a glass rod. There are two general ways in which luster may be decreased—by roughening the surface, that is, changing the physical form of the surface, or by introducing a foreign substance that has a different index of refraction. A mixture of substances with different indices of refraction will reflect light in different directions, thus decreasing the luster of the solid object. The most satisfactory method for delustering nylon consists of making the filaments from a polyamide or a solution of polyamide containing a dispersion of finely divided, inert substances. These substances of course must not react with the polyamide, and they must have an index of refraction different from the polyamide. Examples of such delusterants are titanium oxide, barium sulfate, zinc oxide, and zinc sulfate.

PHYSICAL AND CHEMICAL PROPERTIES OF NYLON

Nylon is a fairly new textile material, and yet its general acceptance by the consumer has been so whole-hearted and so widespread that it constitutes a tribute to the producers and an unspoken recognition of the value of fundamental research in the industrial part of our complicated economy. The more we acquaint ourselves with the facts about nylon textile yarns, the more we are impressed by the imposing list of its desirable properties. Among its outstanding merits are: (1) its extra low density; (2) its uniformly high tenacity and tensile strength; (3) its inherent elasticity, great elongation, and exceptional elastic recovery; (4) its toughness and resistance to abrasion; (5) its very low and uniform shrinkage; (6) its low absorption of moisture and rapid drying; (7) its nonflammability; (8) its ability to be permanently set; and (9) its ability to be dyed rapidly, permanently, and directly with the same dyes ordinarily used for acetate rayon, wool, and silk. Nylon is also distinguished by its great resistance to various agencies: it has extraordinary resistance to almost all chemical reagents and organic solvents; it has good heat resistance; it has good aging characteristics in the air even at high temperatures; it is not attacked by moths or fungi; and it causes no skin irritation. It should be noted, however, that nylon is damaged by strong mineral acids such as HCl and H_2SO_4. It is also attacked by hypochlorite bleach liquor, and, for this reason, if one attempts to bleach discolored nylon fabrics the tensile strength of the goods will be appreciably decreased. Quantitative evidence of many of these statements will be found on the following pages.

DENSITY

Nylon filaments have the lowest density of any substance used for making textile yarns.

Table 46 shows the densities of several textile fibers, together with some other materials which can be made into nontextile filaments.

TABLE 46

DENSITIES OF FIBERS AND FILAMENTS

Material	Density
Nylon	1.14
Boiled-off silk	1.25
Wool	1.30
Acetate rayon	1.30
Raw silk	1.40
Linen	1.50
Cotton	1.50
Ramie	1.52
Viscose rayon	1.52
Cuprammonium rayon	1.52
Steel	7.8
Copper	8.9

When we consider the high tenacity of nylon, as compared with other textile fibers, the importance of this low density becomes more apparent; that is, more strength can be obtained with less weight. If yarns from high-tenacity nylon and from raw silk are made so that the weight is the same (the same denier), the nylon yarns will be about 50% stronger than the silk yarns. Conversely, if nylon and silk yarns are made so as to have the same tensile strength, the silk yarns must be about 40% heavier than nylon. A similar comparison might be made with silk and nylon fabrics. If a steel cable is 1 sq in. in cross-section area it will hold a weight of about 180,000 lb, whereas a similar high-tenacity nylon cable will hold only about 95,000 lb, but the weight of the nylon cable will be only about one-seventh as much as the weight of the steel cable, because its density is so much smaller. If such cables were made so as to have equal tensile strengths, the nylon cable would still be lighter than the steel cable. If we compare nylon with cotton in the same way, we find that the nylon yarn which is twice as strong as cotton yarn will be about 30% lighter than the cotton. Tent cloths made from nylon are durable and strong and yet are lightweight.

TENACITY AND TENSILE STRENGTH

Nylon yarns can be made so that they will have a relatively high or low tenacity. The factors which govern this have already been discussed, and it has been pointed out that increase in tenacity is associated with a decrease in elongation (stretchability). At the present time two types of yarns are manufactured, regular yarns (from 4.5 to 5.0 gm/denier) and high-tenacity yarns (6 to 8 gm/denier). We have already mentioned the connection between density and tensile strength and have called attention to the fact that, strength for strength, nylon is the lightest in weight of any textile material except flax. Table 47 shows this in two ways. The first column shows the tenacity of the fibers in grams per

TABLE 47

PHYSICAL PROPERTIES OF FIBERS*

Dry fibers at 60% R.H.

Fiber	Tenacity, gm/denier	Density	Tensile Strength, lb per sq in.	Tensile Strength ÷ Weight	Grams Weight of 1 m when Tensile Strength is 20,000 lb per sq in.
Acetate ryon	1.4	1.3	23,300	18,000	720
Viscose rayon	1.6	1.52	30,000	20,000	629
Cotton	1.88	1.5	36,000	24,000	536
Silk (boiled off)	3.3	1.25	57,500	46,000	300
Nylon (low-tenacity)	4.8	1.14	70,000	61,000	210
Silk (in the gum)	4.6	1.4	81,000	58,000	220
Nylon (high-tenacity)	6.5	1.14	95,000	83,000	155
Flax	7.2	1.5	140,000	93,000	140

* Shor, *J. Chem. Education*, **21**, 88 (1944).

denier; the second column shows the density of the material; the third column shows the tensile strength calculated from the tenacity. The fourth column is the result of dividing the tensile strength by the density, and these figures show the relative tensile strength expected from equal weights of the various fibers. The last column is the converse of this. These figures have been calculated from the tenacity and tensile strength. These figures are the weight in grams of 1 m of a cable of each fiber of such diameter that its tensile strength will be 20,000 lb per sq in. of cross-section. In this instance, the strength is kept constant and the weight varies.

TABLE 48

WET AND DRY STRENGTH OF FIBERS*

	Tenacity, gm/denier		Per Cent of
	Dry	Wet	Dry Strength
Viscose rayon	1.6	1.0	63
Acetate rayon	1.4	1.0	70
Silk	4.6	3.8	83
Nylon	5.0	4.5	90

* Hoff, *Ind. Eng. Chem.*, **32**, 1560 (1940).

Practically all protein and synthetic fibers lose strength when they are wet. This has been one disadvantage of all the rayons, and for some years much research work has been done in an effort to overcome this defect. Considerable improvement has been made. Table 48 shows the wet and dry strength of four closely related fibers.

ELASTICITY, ELONGATION, AND ELASTIC RECOVERY

All fibers can be stretched if enough tension is applied. This is a physical property inherent in the individual fibers, and therefore among various fibers with their different chemical structures we should expect to have what might be called different stretchabilities. It is well known that wool stretches easily, cotton less easily, and that it is quite difficult to stretch silk very much. Nylon is more easily stretched than any of the textile fibers. If some fibers are more easily stretched than others, then less tension would be required to stretch them a definite amount. The tensions required to stretch various fibers a certain definite amount are known as moduli of elasticity. If nylon is more stretchable than other fibers, its modulus of elasticity should be smaller than that of the others. A du Pont bulletin (1943) gives the results of tests performed in their laboratories. These tests were carried out at a relative humidity of 72%, and the figures (shown in Table 49, second column) are the number of grams tension per denier required to stretch various fibers 1%. This figure is the modulus of elasticity of each of the fibers, in that it is a measure of the elasticity of each fiber reduced to a common size, 1 denier.

TABLE 49

MODULI OF ELASTICITY

Fiber	Modulus, gm	Per Cent of Greater Stretchability than Ramie
Ramie	0.90	...
Silk	0.75–1.16	same
Viscose rayon	0.70	30
Cotton	0.50	80
Acetate rayon	0.40	125
Wool	0.32	180
Unshrunk nylon	0.25	260
Shrunk nylon	0.10–0.15	600

The third column in Table 49 compares the ease of stretch of ramie with that of the other fibers; the figures are expressed as percentages. These figures are calculated by dividing 0.9 by each modulus, subtracting 1, and multiplying by 100.

As fibers are weaker when wet, they should stretch more easily and the modulus of elasticity should be smaller. This means that the relative humidity of the air in which the modulus is determined will affect its size. This is illustrated by the following figures for nylon. At 0% R.H. (bone-dry fibers), the modulus is 0.48 gm/denier; at 50% R.H., it is 0.31 gm; and at 100% R.H. (saturated atmosphere), it is 0.116 gm.

If sufficient tension is applied to fibers, they will stretch until they are broken. The per cent increase in length at the time of rupture is known as the *elongation* of the fiber. Like modulus of elasticity, this is a physical property inherent in the individual fibers. The elongation of natural fibers can be changed very little, except by tricks of plant and animal breeding. However, the elongation of synthetic fibers can be modified considerably by variations in manufacturing technique. If a change of process yields a filament with increased tenacity, the elongation will be decreased. This means that the tenacity and elongation of nylon may vary over a wide range. The same is true of some of the rayons, but with wool, silk, and cotton, the elongation is restricted to a rather small range. The per cent elongation of several fibers will be found in Table 13, page 112.

A material that has any elasticity will have more or less elastic recovery, and an extended discussion of the subject of elastic recovery and the factors influencing it will be found on pages 110 to 116 in Chapter 5. Table 15 (page 115) shows the elastic recovery of some important fibers. The figures show that nylon is outstanding in its ability to regain its original size or shape after having been stretched.

Resistance to abrasion is one of the most important factors determining wearability. Such resistance is a composite of toughness, smoothness, flexibility, and elasticity.

Toughness of fibers is that indefinite inherent property which makes the fibers rugged enough to withstand all sorts of mechanical punishment. Flexibility and elasticity are also inherent properties which depend on the physical arrangement and types of chemical bonds within the fiber. Smoothness in synthetic fibers may be varied by the method of manufacture. Apparently nylon has a high degree of all these essential properties, and it withstands abrasive wear better than silk, rayon, or cotton. This is specially noticeable in the foot area of stockings, where nylon is known to have longer life than the other fibers.

The *shrinkage* of nylon under ordinary conditions is low. Most fibers will swell when immersed in such liquids as water, glycerin, or sodium hydroxide solution, but nylon shows no swelling when treated in this way. In the du Pont laboratories, yarns were given treatments with water at various temperatures for various lengths of time. These tests were made on two kinds of yarns, completely unshrunk yarn (pirns), and yarn which had been partially shrunk (sized cones). The twist had been set in the latter by holding it at about 75° C for 2 hours. The results are given in Table 50.

The *moisture regain* of nylon is lower than that of any of the textile fibers if compared at the same relative humidity. Regain is the per cent moisture over and above the bone-dry weight that textile materials will absorb when exposed to an atmosphere of some designated relative humidity. It is not the per cent moisture in the material at that time, but the per cent moisture based on the bone-dry material (see page 119).

If we start with a bone-dry fabric and expose to a relative humidity of 40%, it will absorb a certain amount of moisture; that is, an equilibrium will be established between the moist fabric and the surrounding atmosphere. The amount of moisture absorbed is a characteristic of each type of fiber, but it may be changed considerably by various finishing treatments given yarn or cloth.

TABLE 50

SHRINKAGE OF NYLON

	Shrinkage, %			
	In Pirns		In Sized Cones	
Treatment	Actual	Residual	Actual	Residual
25° C water, 3 minutes	4.8	4.2	0.3	4.1
80° C water, 3 minutes	7.4	1.0	2.2	1.2
100° C water, 3 minutes	8.8	0.2	3.6	−0.1
100° C saturated steam, 3 minutes	7.5	1.1	3.5	0.8
100° C saturated steam, 10 minutes	8.4	0.4	3.6	0.6
100° C saturated steam, 30 minutes	8.4	0.4	4.4	0.4
15 lb saturated steam, gauge 3 minutes	9.7	0.3	5.4	0.3
15 lb saturated steam, gauge 10 minutes	10.0	0.2	5.8	0.0
30 lb saturated steam, gauge 3 minutes	11.5	0.2	7.3	−0.2

If the same fabric were exposed to 65% R.H. (a higher concentration of water vapor in the air), the cloth would absorb more moisture before the equilibrium was established; that is, the regain would be greater. The relation between humidity and the regain of nylon is shown in Table 51. These figures were determined in the du Pont laboratories and published in a bulletin in 1943.

As previously stated, nylon has a lower regain than other fibers. This is shown by the figures in Table 52, which are the regains of various fibers at a relative humidity of 65% after equilibrium has been established. The rate of regain, or the time required for reaching equilibrium, is a different matter. This depends largely on the size of yarn, whether it is loose in skeins or wound tightly on cones, spools, or bobbins, or whether it is cloth or knit goods. An unfinished nylon fabric will reach equilibrium at 72% R.H. in about 20 minutes, no matter whether it is very dry or at a high humidity to begin with. A 500-yd skein will require about an hour to reach equilibrium, and nylon yarn wound on a cone may require a couple of days.

TABLE 51

REGAIN OF NYLON, AS AFFECTED BY HUMIDITY

Relative Humidity	Regain, %
10	1.1
20	1.4
30	1.7
40	2.3
50	2.8
60	3.4
70	4.1
80	5.0
90	5.7
97	6.2

There are some practical points connected with the water-absorbing capacity of fibers. The lower the regain of a type of fiber, the faster it will dry. Since nylon has the lowest regain, it should dry more quickly than other fibers. When fibers have a low regain, they tend to accumulate static electricity. Thus nylon should be handled (twisted, woven, etc.) in an atmosphere of high

TABLE 52

MOISTURE REGAIN OF FIBERS

Fiber	Per Cent of Regain at 65% R.H.
Nylon	3.8
Acetate rayon	6.0
Cotton	7.5
Linen	8.0
Silk	11.0
Mercerized cotton	11.0
Viscose rayon	12.0

relative humidity. On the other hand, it is advantageous to increase the water-absorbing capacity of some materials. This makes them heavier and may give them a better hand or feel. This is one reason why cotton goods are finished with a hygroscopic substance of some sort.

Nylon can be given a more or less *permanent setting.* This means that nylon fabrics or knit goods may be made to take a certain dimensional form or shape and retain it permanently, no matter how they may be treated, unless the conditions of the original setting are exceeded. This makes possible a sort of preforming by which knit goods or fabrics may have their forms established by setting and then retain them permanently, and even though the form may be temporarily distorted it will come back to the original shape.

Setting is done by means of heat, either dry or moist. Dry heat setting is not very satisfactory because (1) it is not so permanent as moist heat setting, and (2) there is danger of damage to goods by local overheating. Moist heat setting is accomplished by means of hot or boiling water or live steam with pressure. The process is similar to pressing men's wool trousers, with a hot iron through a damp cloth. This not only takes out wrinkles but also puts in a crease. The wool is set in this shape and retains it, but wool does not have as high a degree of permanent set as nylon and will reverse in a shorter time. In fact water alone will remove the set imposed upon wool, cotton, and other fibers, but it will not remove the set given to nylon.

The cause of the permanent setting property of nylon is not clearly understood, but it may be due to a readjustment or rearrangement of molecules in nylon to a molecular structure which is under less strain. You will recall that, when nylon is made, it is cold-drawn in order to obtain certain desirable results. During this drawing operation, molecules are taken from their random arrangement and oriented or lined up more or less parallel. The application of heat may relieve some of this strain so that there is no necessity for the molecules to change their position.

Setting of nylon is a function of heat, moisture, and time. For example, if a nylon fabric is set with boiling water (100° C), it can be washed and twisted and wrinkled at a temperature of 80° C and still come back to its original shape. But if it is pressed or wrinkled at a temperature of 115° C, it will not go back to the original shape because the conditions of the original setting have been exceeded and a new setting accomplished, and if creases or wrinkles are present when this new setting takes place they will be permanent. Nylon fabrics should never be washed in hot water unless they have previously been set at a higher temperature. However, if such an undesirable situation occurs, its effects can be eliminated by the use of higher temperatures and an intentional new setting.

When full-fashioned nylon stockings are preboarded, they are mounted on metal forms of suitable shape, and these forms are heated externally with live steam for about 1 to 3 minutes. This shrinks the nylon slightly, and the contracted stockings take the shape of the form. The heat and moisture set them in this form, and after this setting they can be washed repeatedly and still retain their size and shape. The beauty and clarity of the stitch characteristics of nylon hosiery are made permanent by such a preforming or setting treatment. The contraction of the stockings on the metal form opens up the mesh and smooths out irregularities, and since they are set in this form the overall stitch appearance of the stockings is improved. However, if the knitting has been poorly done, the defects will show up more clearly.

Another practical use of nylon's setting property is found in making upholstery fabrics and transparent velvet. If the pile of upholstery is set with live saturated steam under pressure, it will be highly crush-resistant. Likewise, pressure-set transparent velvet can be washed and dried without brushing up the pile.

Nylon has extraordinary resistance to most chemical reagents, especially organic compounds. It is inert to organic reagents such as aldehydes, ketones, alcohols, soaps, and many organic acids. However, it will dissolve in boiling 85% acetic acid. It gradually deteriorates when heated in benzoic acid, oxalic acid, or orthophosphoric acid. Ordinary organic solvents, such as gasoline, benzine, chloroform, carbon tetrachloride, and trichloroethylene, have no effect on nylon. There are several known solvents for nylon. Among the best are concentrated formic acid and the phenols: phenol (carbolic acid), metacresol, xylenol, and cresylic acid. Some other solvents are a hot 20% solution of $CaCl_2$ (saturated) in methanol, benzyl alcohol at the boil, trichloracetaldehyde, and hot ethylene glycol.

With certain inorganic reagents nylon is somewhat more reactive.

Caustic alkalies have no effect on it (different from the natural protein fibers), and it may be heated at 85° C in 10% NaOH solution for 16 hours with no apparent disintegration.

Nylon loses strength when treated with ordinary oxidizing agents or mineral acids. Cold concentrated HNO_3 rapidly disintegrates nylon, and boiling 5% HCl causes nylon to become brittle and ultimately destroys it. Normal solutions of HCl or H_2SO_4 will cause nylon yarn to lose about 16% of its strength in 10 minutes, and 0.1 N solutions of these acids will do the same thing in 3 days.

The *heat resistance* of nylon is satisfactory, especially in the absence of oxygen. If stored in the dark for 4 months at 65° C, in air, a loss of 5% in strength is found, and if stored for a year, a loss of 20% results. A temperature of 200° C has no effect on nylon yarn after 3 hours in an oxygen-free atmosphere, but at 225° C for 3 hours some loss in a strength is found. At 245° C there is considerable loss in strength.

The heat resistance of nylon can be demonstrated by ironing. When ironing nylon any temperature up to 180° C is perfectly safe. Before this temperature is reached, all unset wrinkles will have been removed. Above 180° C the material begins to get sticky, and at 230° C serious damage begins.

High temperature and dry air will discolor any fiber. The familiar scorch on cotton is a good example. To test the effect of dry heat on some of the common fibers, they were maintained in dry air for 5 hours at 150° C. Cotton was affected the least, turning a barely noticeable yellow. Viscose and acetate rayon showed slightly more yellow, nylon a little more, and wool a decided yellow. With this treatment silk was discolored the most, giving a definite brown color.

SEPARATION OF NYLON FROM OTHER FIBERS

Natural protein fibers (wool and silk) and acetate rayon are destroyed by hot NaOH, but vegetable fibers and nylon are not affected by such treatment. Acetate rayon is soluble in acetone, whereas other fibers are not. Silk and viscose and cuprammonium rayons are dissolved by concentrated $Ca(CNS)_2$ at 70° C, but nylon is not. Boiling 85% acetic acid will dissolve nylon, but cotton and linen are not affected.

On the basis of these facts, nylon can be separated from other fibers by the following means: from acetate rayon by use of acetone; from cotton and linen by use of boiling 85% acetic acid; from viscose and cuprammonium by use of concentrated $Ca(CNS)_2$, and from wool and silk by the use of hot NaOH.

USES FOR NYLON

Suitable and practical uses for any textile fiber must be based on its physical and chemical properties. Nylon has established its reputation and has come to stay, because of its use in the hosiery trade. Not only have nylon stockings replaced silk stockings, but they have surpassed silk hose in many qualities, such as sheerness, durability, lightness of weight, and quick-drying property. The 15 denier nylon monofilament yarn can be used to make the sheerest of stockings, which have satisfactory strength and wear resistance.

If we consider the physical properties in which nylon equals or surpasses other textile fibers, we shall find that it is suitable for many uses other than hosiery manufacture. Among these physical properties are high tensile strength coupled with light weight, exceptional elasticity and resiliency, abrasion resistance, low absorption of moisture (quickness of drying), and permanent set.

Many fabrics such as marquisette and chiffon must be sheer and lightweight and yet must be strong enough to be practical. Nylon is an ideal material for making such fabrics. The same may be said about cloths for foundation garments, where strength is essential and light weight or small volume desirable.

Because of the high elasticity and resiliency of nylon yarn, we find it being used in a great variety of textile materials. Nylon stockings will accommodate themselves to knee flexing and retain their original shape better than any other fiber. This is partly due to the natural elastic recovery of nylon and partly to the fact that the shape of the stockings has been set.

A nylon fabric will regain its original shape not only after being stretched but also after being compressed. This is because of the resiliency of nylon yarns. This property is very important in the production of plushes, transparent velvets, wrinkleproof neckties, and upholstery fabrics. The abrasion resistance of nylon makes it suitable for all sorts of pile fabrics.

A permanent set can be imposed upon nylon fabrics or knit goods. This very valuable property is responsible for many uses for nylon yarn. Nylon stockings which have been set to a definite shape will tend to regain such shape after any mechanical distortion. Thus nylon stockings do not bag at the knees, and after washing, when hung up to dry, they not only dry quickly but assume a flat, neatly pressed appearance. This is because the stockings were set in this shape by steam under pressure when they were manufactured. It is easy to set pleats in nylon skirts with a steam iron, and nylon curtains which have been set will not shrink or sag after washing.

Nylon is finding a wide use in blending with other fibers. Every day we use many textile products that do not possess all the properties we would like them to have. We would, for instance, like overcoats with adequate warmth but less weight; cool, light summer clothes that would not lose their fresh, clean appearance on hot, sticky days; fabrics that would wash readily and dry quickly.

Textile designers are always trying to produce new materials to meet such needs. In some instances they find that a yarn made of one fiber is best suited to their purpose. In others, a combination or blend of two or more fibers is required to give a fabric all the properties it should have.

These designers find nylon yarn very valuable. In one or another of its forms, it can be easily combined with other fibers to make new or greatly improved materials.

Continuous-filament nylon and rayon yarns, for instance, are used together to make many fabrics. Such materials can be designed to have both the draping qualities and hand, or feel, of rayon together with strength, abrasion resistance, and washability of nylon.

Blending wool and nylon staple fibers produces yarns with many desirable properties. Even a little nylon greatly increases the strength of the yarn compared to wool alone. This strength makes possible finer yarns and, in turn, sheer fabrics which have the look, feel, and warmth of wool plus the abrasion resistance and durability of nylon. The proportion of each fiber can be varied to bring out the properties most important for a particular use.

Similarly, nylon can be blended with cotton. Again, strength and abrasion resistance increase without loss of cotton's characteristic softness.

In this way nylon combines with other fibers to increase the variety of fabrics that can be tailor-made for specific uses. More and more textile articles are being made of fiber blends so that they may have the particular properties we want them to possess.

Nylon wool is an interesting novelty. It is made by cutting continuous-filament nylon into staple the length of wool, packing it into bales, and heating with steam. This puts a wool-like crimp into the fibers, and the heat sets it. It can then be spun into yarn suitable for sweaters. The high elastic recovery of nylon and its dimensional stability in laundering (resistance to shrinkage) make it especially suitable for such purposes.

In the nontextile field the uses for nylon are even more varied. Some of these applications were developed because of the emergencies of World War II. It was found that nylon cords for heavy bomber tires and heavy-duty truck tires were more satisfactory than any other cords. Nylon ropes were used for lifting gliders from the ground. Such a rope ½ in. thick will lift a weight of 3 tons, and because of nylon's stretchability the glider is lifted with a minimum of shock.

Nylon monofilament can be used for all sorts of brushes (tooth, hair, clothes, and paint brushes), window screens, and tennis racket cords. Nylon screening can be made in any color desired; it needs no painting and will withstand the action of any weather. Tennis rackets made with nylon cords need not be protected from water. Nylon can be used for wrapping insulated electric wire and for making fish lines, dental floss, and surgical sutures. It can also be extruded in a thin film suitable for photographic films, which are thinner and lighter weight than the ordinary film.

WASHING AND SCOURING NYLON

The nylon finisher and the housewife have different problems in the cleaning of nylon goods. Before nylon yarns are knitted or woven, they are usually sized and oiled in order to facilitate the making-up operations. Before the finisher can dye and finish the goods, he must remove not only the size and oil but also any other grease and dirt that may have been picked up during the various mill operations. The process by which this is done is called scouring. The problem of the housewife is somewhat simpler. The dirt which accumulates on nylon stockings and garments is a mixture of perspiration salts and body oils which have trapped dust from the air. Perspiration salts are soluble in water, and body oils are quite easily emulsified, so that the cleaning of such fabrics is not difficult.

There are various mechanical ways for scouring nylon goods, but all of them involve a scouring bath which usually consists of about 2% olive oil soap and 1.5% trisodium phosphate (or similar detergent), to which 2% of a Gardinol type of detergent may be added (see page 79). High-molecular-weight alcohol sulfates are not essential, but if they are not used the amount of soap should be increased. The above percentages are based on the weight of goods to be scoured and do not designate the concentration of solution used. The weight of bath should be from 20 to 30 times the weight of goods. The temperature of the scouring bath may vary from 80° C to the boiling point, but it is best to keep it below the boil in order to avoid the possibility of setting wrinkles in the fabric.

There are two situations in which a prescouring soaking treatment is advisable. Some types of greases are especially hard to remove from nylon; here a soaking treatment is of help. Sometimes oil or dirt may have been fixed in the nylon during some setting treatment. Here again scouring will be more efficient if the goods are soaked for some time before scouring. The consumer may also be faced with the same problem, and a knowledge of what to do is an advantage.

A soaking treatment should be carried out as follows: The goods are immersed in a short bath, that is, one where the ratio of bath to goods is about 20 to 1. The bath contains 5% good olive oil soap, 2% Gardinol, and 0.25% trisodium phosphate. The goods are entered at about 75° C, impregnated thoroughly, and let stand for 5 or 6 hours, the bath being allowed to cool down of its own accord. At the end of this time the goods should be agitated so as to wash them, or they may be transferred to a regular scouring bath. This operation will loosen solid dirt particles, or even dirt-containing globules of grease, which will rise to the top of the bath. If these particles are not removed before rinsing, they may be deposited on the goods and prevent a good job of cleaning. A simple way to avoid a deposit on the goods is to add cold water to the bath until it overflows. As it overflows, the insoluble dirt particles will also overflow, so that their redeposition on the goods is prevented. After this, the material may be rinsed as usual.

Whenever nylon is washed, the temperature must be watched. If the temperature is too high a new set may be imparted to the material, and if this happens while the goods are badly wrinkled the results will not be desirable, because the wrinkles may be more or less permanently set and very hard to get out.

The consumer may wish to remove grease stains from nylon by the use of organic solvents. It is fortunate that nylon is so resistant to such a treatment. It is unaffected by such solvents as benzine, naphtha, gasoline, acetone, alcohol, and chlorinated hydrocarbons, such as chloroform and carbon tetrachloride. These solvents will remove ordinary grease spots, unless they have been set in the goods, in which event a long soaking treatment should be applied. If the solvents contain chlorine they should not be old or much used. Sometimes free hydrochloric acid will have been formed, and if nylon is cleaned with such solvents it is likely to be damaged by the mineral acid.

Nylon should never be bleached with chemicals like Clorox or Roman Cleanser after washing. Remember that bleaching will not remove dirt. It is a decolorizing operation and not a detergent. Nylon itself is very white and should require no bleaching before dyeing. Since nylon is discolored by oxidizing agents containing chlorine, ordinary hypochlorite should not be used. Not only will the nylon be discolored instead of whitened, but it will be rendered considerably weaker. Peroxide bleaches do not discolor nylon but do weaken it.

In connection with washing and cleaning nylon, reference should be made to the ironing of nylon materials (see page 329).

QUESTIONS

1. What man's name and what manufacturing company are associated with the discovery and development of nylon?

2. Make a statement that will define in scientific terms what nylon is.

3. When was nylon put on the market?

4. From what two chemical compounds is nylon (fiber 66) made? State briefly how it is made.

5. What is meant by the term "condensation" when applied to a reaction between two chemical compounds? What is a condensation polymer? a linear polymer?

6. What is the first product of the reaction between adipic acid and hexamethylene diamine? Write the formula for the product obtained by the action of one molecule of each. Does this compound ionize? Show the ions.

7. What is formed when an ammonium salt of an organic acid is strongly heated? Show the reaction with ammonium acetate. Show it with hexamethylene-diammonium adipate.

8. Explain how it is possible for the above adipamide to react with more adipic acid and hexamethylene diamine.

9. What is the structural unit of nylon (fiber 66)?

10. How can a superpolyamide be made from a polyamide?

11. What is the chemical difference between nylon flakes and nylon filament? Tell how each is made.

12. Tell how adipic acid is made, starting with chlorine and benzene.

13. Tell how hexamethylene diamine is made, starting with adipic acid.

14. What is accomplished within a nylon filament by cold drawing? How does this change the physical properties of the filament?

15. In how fine a denier can nylon filaments be made? What is the highest denier in which they are made?

16. What are some of the standard sizes of nylon yarns, and how many filaments are twisted together to make each of them?

17. What is the average tenacity of standard nylon yarns? of high-tenacity yarns?

18. Compare nylon with other textile fibers with regard to (*a*) specific gravity, (*b*) elongation, (*c*) elastic recovery, and (*d*) regain of moisture.

19. How can nylon stockings be set? What has this operation to do with their holding their shape? Under what conditions could the shape be changed so as to retain the new shape?

20. How is nylon affected by: 10% NaOH, concentrated HCl, concentrated HNO_3, boiling 85% acetic acid, ordinary oxidizing agents, heat (ironing), ordinary dry cleaning solvents?

21. How can nylon be separated from (*a*) cotton, (*b*) wool and silk, (*c*) acetate rayon?

22. What physical properties of nylon make it very desirable for use in hosiery, upholstery, chiffons, window screening, slips, and foundation garments, plushes, and marquisettes?

12 · Man-Made Polymerized Filaments: Vinyon, Saran, and Orlon

Polymerization is a reaction in which many molecules of the same or different compounds unite to form one very large molecule with certain fragments, derived from the original reacting substances, repeated in the skeletal structure of the large molecule. Carothers has defined polymerization as "the intermolecular combinations of small molecules which are functionally capable of proceeding indefinitely." The old idea of polymerization was a reaction taking place between many molecules of the same substance to form a polymer the molecular weight of which was a multiple of the monomer. This definition is no longer adequate, because we know that many polymers are formed from mixtures of compounds, not only by simply adding together, but also by condensation reactions in which simple molecules like water or ammonia are lost. We found that nylon is such a polymer. Nature is a great manufacturer of high polymers, most of which are amorphous substances like rubber, cellulose, proteins, starch, and asphalt. Man has synthesized high polymers for a long time, but since 1925 a great stimulus has been given to such syntheses because new and important uses for the resulting amorphous resins have been discovered. Most of them have been based on the fact that these resins can be plasticized. Thus man has not only synthesized high-polymer resins but also has learned how to change them into plastics.

We have learned that nylon is produced by condensation polymerization, but there are other types of polymerization, on one of which the manufacture of Vinyon, Saran, or Orlon is based. This is simple ~~addition polymerization in which~~ small molecules of one or more compounds merely add to each other to yield a high polymer. We can divide addition polymerization into three groups, (*a*) simple polymerization, (*b*) copolymerization, and (*c*) heteropolymerization.

In simple polymerization, many molecules of the same compound add to each other to form long chains in which the original skeleton is repeated time after time. This is typical of the simple ethylenic compounds like ethylene, $CH_2{=}CH_2$, and vinyl chloride, $CH_2{=}CHCl$. If several molecules of vinyl chloride add to each other, the resulting chain will be

$$—CH_2—CHCl—CH_2—CHCl—CH_2—CHCl—, \text{ etc.}$$

At present we are not concerned with the question of what is attached to each end of the long chains. The structural formula for the polyvinyl chlorides can be represented by $(—CH_2—CHCl—)_n$, where n is a large number.

If two ethylenic compounds are mixed and then caused to polymerize, a copolymer is formed. Suppose ethylene and vinyl chloride were mixed in equal amounts and polymerized in a perfectly symmetrical way. The polymer would have the following structure;

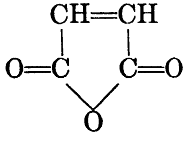
$$—CH_2—CH_2—CH_2—CHCl—CH_2—CH_2—CH_2—CHCl—CH_2—CH_2—$$

and the repeated unit would be

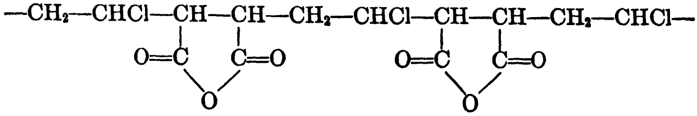
$$(—CH_2—CH_2—CH_2—CHCl—)$$

However, we have no assurance that perfect symmetry is attained, and it is reasonable to assume that some portions of a chain will consist of repeated vinyl chloride or ethylene fragments. Such a situation would surely be true if unequal amounts of the monomers were mixed. It is seen that copolymerization takes place between two different molecules each of which could polymerize by itself.

In heteropolymerization two different molecules add to each other to form long chains, but one of them cannot be polymerized by itself. An example of such a type is the polymerization of mixtures of vinyl chloride and maleic anhydride.



Maleic anhydride is structurally capable of polymerization, but it will not polymerize. However, vinyl chloride can be added to it, and a high polymer can be produced:



The Vinyl Family of Resins: The Polyvinyls

All the members of this group can be considered polymers or copolymers of compounds containing the vinyl group, $CH_2{=}CH{-}$, or its equivalent. Among such compounds being used for the manufacture of resins and textile filaments are vinyl chloride, $CH_2{=}CHCl$; vinylidene chloride, $CH_2{=}CCL_2$; vinyl acetate, $CH_2{=}CH{-}O{-}CO{-}CH_3$; and acrylonitrile, $CH_2{=}CH{-}CN$. We shall discuss three of these resins and the filaments made from them. These are Carbide and Carbon's Vinyon and Vinyon N, Dow's Saran, and du Pont's Orlon.

VINYON AND VINYLITE RESINS

Vinyon and Vinylite are names registered as trademarks designating products of the Carbide and Carbon Chemicals Corporation. This company started general research in this field in 1927, and in 1933 began to concentrate on the uses for vinylite resins in the field of textiles. The result was Vinyon resin, a copolymer of vinyl chloride and vinyl acetate, and in 1939 the American Viscose Corporation was licensed to fabricate filaments and yarns from this resin. Thus Vinyon was the first synthetic plastic filament to be produced on a commercial scale in this country.

The vinyl resins are made from all possible combinations of vinyl chloride and vinyl acetate, each combination of which has its own special properties. It was found that the copolymer made from 88% vinyl chloride and 12% vinyl acetate was suitable for filament production and use in textile materials. Polyvinyl chloride is much too rigid, has too high a melting point, and is too tough to be of much value. In order to convert it into a plastic, it is necessary to add plasticizers, which are usually high-boiling liquids, waxes, gums, etc. But resins plasticized in such a way are always subject to a change in composition over a period of time, due to loss of plasticizer by evaporation, oxidation, or solvent action. On the other hand, polyvinyl acetate is too soft, has too low a softening point, and is too soluble. However, mixtures of these two form a copolymer which is just right. The polyvinyl acetate seems to plasticize the rigid, hard, high-melting polyvinyl chloride, so that no additional plasticizer is necessary. This is quite important because it means that when vinyl chloride and vinyl acetate are polymerized to form Vinyon there is no chance for a change in composition.

In the manufacture of Vinyon the polymerized resin is dissolved in acetone, and the solution extruded through spinnerets downward through tubes into which warm air is passed. This causes the evaporation of the solvent, acetone (b.p. = 56.5° C), and the formation of filaments of Vinyon. After this, the yarn is oriented by stretching, as in the manufacture of nylon (page 319). The greater the amount of stretch imposed on the yarn, the greater the strength will be, but this stretching is associated with a decrease in elongation and elasticity. Regular Vinyon (commercial grade = ST) is stretched about 200% and has a tenacity of 2.0 to 2.8 gm/denier, whereas high-tenacity Vinyon (HST) is stretched about 400% and has a tenacity of 3.5 to 4.0 gm/denier.

Vinyon yarn has several desirable properties. It has sufficiently good strength, wet as well as dry. It is impervious to water, and even at 95% R.H. will absorb only 0.1% moisture. It has good elongation, but its elastic recovery is not too satisfactory. It is not affected by molds or mildew. It is not attacked by concentrated mineral acids, strong alkalies, or oxidizing agents. It will char and melt but is not flammable.

However, it has some undesirable properties. Because of its hydrophobic nature it cannot be dyed by conventional methods. The main objections to it are its poor dimensional stability at elevated temperatures (it shrinks at 75° C) and the fact that it becomes sticky at higher temperatures. It should not be heated above 65° C. This means that it cannot be boiled in water or ironed like other goods. This high thermoplasticity has been turned to advantage by using it as a binder in cotton, wool, and glass felts and in hat manufacture.

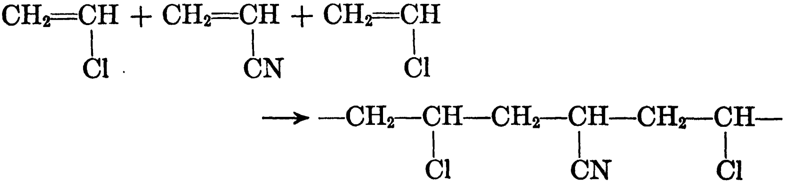
VINYON N

Carbide and Carbon continued research in an effort to produce a resin that would yield filaments superior to Vinyon in resistance to heat and shrinkage. One of the results was the granting of U.S. Patent 2,420,330 (1947) for the manufacture of a new resin which was called Vinyon N. This resin is a copolymer of vinyl chloride with acrylonitrile which can be converted into filaments that are much better than Vinyon.

Vinyl chloride will polymerize to form a resin that is only partially soluble in acetone. Polyacrylonitrile, obtained by the polymerization of acrylonitrile, is completely insoluble in acetone. The strange fact is that, when these two vinyl compounds are copolymerized to form a resin in which the vinyl chloride content ranges from 40 to 80%, the resin is soluble in acetone. It appears that the monomers plasticize each other.

It is found that these two vinyl compounds do not copolymerize at the same rate, but the acrylonitrile copolymerizes faster than the chloride. Thus the percentage of nitrile in the resin will always be greater than its percentage in the original mixture of monomers. Another way to think about it is that the nitrile disappears from the monomer mixture faster than the chloride does. As a consequence, if a uniform resin is to be produced from a definite monomer mixture, more vinyl chloride must be added to the polymerization vessel at intervals. The resin used for making textile filaments contains 56 to 60% copolymerized vinyl chloride; this requires the original monomer mixture to be about 92% vinyl chloride.

The copolymerization of these two vinyl compounds is simple addition polymerization, illustrated by the following equation:



$$\underset{\displaystyle\text{Cl}}{CH_2{=}\underset{|}{CH}} + \underset{\displaystyle\text{CN}}{CH_2{=}\underset{|}{CH}} + \underset{\displaystyle\text{Cl}}{CH_2{=}\underset{|}{CH}} \longrightarrow -CH_2-\underset{\underset{\displaystyle\text{Cl}}{|}}{CH}-CH_2-\underset{\underset{\displaystyle\text{CN}}{|}}{CH}-CH_2-\underset{\underset{\displaystyle\text{Cl}}{|}}{CH}-$$

As the resin does not contain equal proportions of the two compounds, there can be no actual repeated unit in the long-chain polymer.

When Vinyon N resin is made, a polymerization autoclave is charged with 92 parts of vinyl chloride and 8 parts of acrylonitrile, together with small amounts (0.5 to 1.0%) of catalyst and emulsifying agent and 300 to 400 parts of water. Suitable catalysts are potassium persulfate, hydrogen peroxide, or benzoyl peroxide. Among the several well-known emulsifying agents which are satisfactory are sodium lauryl sulfate and its homologs. The mixture must be kept under pressure because vinyl chloride (b.p. = −13.9° C) is a gas at ordinary temperature and pressure. The mixture is stirred to form an emulsion and the temperature is raised to about 40 to 50° C and kept there for several hours. More vinyl chloride is added at intervals of about 4 hours. At the end of the polymerization period, the emulsion is broken by adding an equal volume of acetone; then the resin is allowed to settle and is filtered off, washed, and dried. It is a powder varying in color from light cream to amber. Vinyon N yarn is spun by dissolving the resin in hot acetone, filtering, deaerating, and forcing the solution through spinnerets into long tubes, where the acetone is evaporated. This produces yarn with filaments of about 10 denier each. It has a high elongation, but its tenacity is only about 0.7 to 0.9 gm/denier, and it shrinks about 25% when heated.

The strength of Vinyon N can be greatly improved by stretching, which orients the long polymer chains in a parallel alignment. The stretching is done with steam or hot air at temperatures ranging from 110 to 170° C. The greater the amount of stretch, the stronger the yarn will be and the smaller the denier of individual filaments. Stretching more than 2000% has yielded filaments of about 0.35 denier. The two most suitable amounts of stretch are 900 and 1300%, giving filaments of 0.75 to 2.0 denier.

Stretched Vinyon N yarn will shrink at temperatures above 65° C. For example, dry yarns will shrink 8.5% at 80° C, and 15% at 100° C; wet yarns will shrink 13% and 21% at these temperatures. For some purposes, such as crepe effects, this shrinking property is desirable, but for general textiles it is not advantageous. However, this shrinkage can be controlled and the dimensional stability of the yarns improved by a heat modification treatment.

Vinyon N yarns may be stabilized by holding them at 110° C for 6 hours, after which they will not shrink at temperatures up to 100° C, and even at 120° C the shrinkage is only 2% (37% if wet). After being stabilized at 150° C for 3 hours, the yarn may be heated to 120° C and show no shrinkage when dry and only 6% when wet. This means that stabilized Vinyon N yarns or cloth may be subjected to any laundering operation without danger of shrinkage.

PROPERTIES OF VINYON N

Vinyon N is a cream to amber colored yarn with a specific gravity of 1.3; it absorbs less than 0.5% water; it will not burn except in the presence of a direct flame, and it will be self-extinguishing when the flame is removed.

Since Vinyon N yarns can be made in several different qualities, by different finishing treatments, we should expect the tenacity and elongation to vary. The figures for the yarn being manufactured in 1948 were: oriented (stretched) yarn, tenacity 4.2 gm/denier and elongation 10%; oriented and heat-stabilized yarn, tenacity 3.5 gm/denier and elongation 23%. The wet strength is the same as the dry strength. Elastic recovery is from 90 to 93%.

When Vinyon N yarns are oriented by stretching, considerable strain is imparted to the filaments. When the yarn is gradually heated, a temperature is reached at which this strain begins to be released and the yarn starts to shrink. As the temperature is increased, more release of strain occurs, together with more shrinkage. When a yarn has had its strains relieved at some definite temperature, it will be dimensionally stable (will not shrink) at any temperature below this. Heat may be applied to Vinyon fabrics at temperatures below the strain release temperature in order to shape them, as in boarding hosiery or pressing in creases. This shaped fabric is not changed by wetting, and the shapes are relatively permanent until the shaping temperature is equaled or exceeded.

Vinyon N is exceptionally resistant to concentrated mineral acids and caustic alkalies and is not affected by strong oxidizing agents below 50° C. It is insoluble in all common organic solvents, especially when heat-modified.

The Vinylidene Resins: Saran

Vinylidene resins are made by the copolymerization of vinylidene chloride with vinyl compounds such as vinyl chloride and vinyl acetate. The resin most suitable for filament extrusion for the textile industry is made from vinylidene chloride and vinyl chloride. The raw materials and monofilaments of vinylidene resins are made by two companies, the Dow Chemical Company, where the basic raw resin is made under the trademark Saran, and the Firestone Industrial Process Company, which produces the monofilament under the trademark Velon. Although monofilaments are being made and used for many purposes, experimental work on multifilament yarns is still being carried out, and the use of vinylidene resins in the field of textiles will probably be greatly extended.

The fact that vinylidene chloride could be polymerized has been known since 1920, but it was in 1930 that the Dow Chemical Company started an extensive investigation of the possibilities of applying this knowledge in the field of plastics, and since that time over fifty patents have been assigned to the company covering all phases of the manufacture and fabrication of Saran. The well-known Dow research methods were followed during this period, with the result that we now have a plastic fiber with outstanding properties for certain specialized uses. Saran is similar to Vinyon, and although it has not yet been made in as small denier filaments as Vinyon, the two filaments will probably become competitors in certain textile fields. Both products have a high resistance to the action of corrosive chemicals and solvents and are water-repellent, tough, and resistant to mechanical abrasion.

Saran is a long-chain high polymer made by the copolymerization of vinylidene chloride with vinyl chloride. It is not a condensation polymer like nylon but is like Vinyon (see page 340).

If vinylidene chloride is allowed to stand for 40 hours at 45° C with about 0.5% benzoyl peroxide, it will polymerize to the extent of about 95%. Long-chain molecules are formed with a structural unit, $—CH_2—CCl_2—$, until molecular weights of 10,000 to 100,000 are obtained. The polyvinylidene chloride is a hard, rigid solid which has a softening point of 185 to 200° C. This high softening point greatly restricts its use, and it would be quite impractical for textile purposes. So it is copolymerized with vinyl chloride. The molecules of the monomers simply add to each other to form long chains such as

$$—CH_2—CCl_2—CH_2—CHCl—CH_2—CCl_2—CH_2—CHCl—$$

It is hardly possible that the polymer is as symmetrical as this, especially when it will contain an excess of vinylidene chloride. Several molecules of vinylidene chloride will add to each other, and then one or two vinyl chloride molecules will enter the chain, and even though this is a random addition the proportion of the two monomers in the completely copolymerized product will be the same as the proportion in which they were originally mixed.

When vinylidene chloride is copolymerized with vinyl choride, a whole series of products with graduated properties can be made, depending on the proportion of the two compounds and on time and temperature. By using mixtures containing from 10 to 30% vinyl chloride at temperatures of 30 to 45° C, it is possible to make resins with softening points ranging from 80 to 170° C. The resin used for making the monofilament Saran has a softening range of 115 to 140° C and a molecular weight of about 20,000. Catalysts for the copolymerization are similar to those used for making the vinylite resins (Vinyon).

EXTRUSION AND FABRICATION OF SARAN

Let us first consider briefly the machinery, the extrusion technique, and the various steps in the process, and then discuss in more detail the reasons for some of the conditions and operations, based on the fine structure of the vinylidene resin.

The resin is fed into the spinning machine in powder or granular form and is carried at a uniform rate to the extrusion die by means of a horizontal traveling screw. As the resin approaches the die, through which it is to be forced in filament size, it is heated above its softening point so that it is thoroughly melted and thus is extruded in a quite fluid form. Extrusion temperatures run from 160 to 180° C. Note that Saran is extruded through a die that has one opening, and not through a spinneret as in spinning rayon and nylon filaments. Rayon and nylon are spun in multifilament form, but Saran is spun as a monofilament. The size and shape of the die determine the dimensional quality of the product. Saran is sensitive to high temperatures, and its decomposition is catalyzed by iron- and copper-base metals. For this reason those parts of the extruder which are hot must be made of magnesium alloy or nickel. After leaving the die, the material passes into a bath of water at about 10° C (the quenching operation). The strand is drawn through the water by being wound onto a take-up roller at such a rate that the proper cooling time is provided. It is then passed to a second roller (the orienting or stretching roller) which revolves at a higher speed than the first roller and thus accomplishes the 400% stretching given the material, as a result of which its strength is greatly increased by the orientation of the long-chain polymer molecules. After the stretching operation, the monofilament is drawn off by any suitable winding equipment.

Now let us look at the inside of the polyvinylidene resins and see how they can be changed and, in consequence of such change, take on different physical properties. This brings us to the fine structure of the resin, the arrangement of molecules within the solid, and their relative positions with respect to each other. The solid state of matter can exist in two forms, amorphous and crystalline, and since vinylidene resins can exist in both these forms we must have a clear concept of the difference between them. The amorphous state, as illustrated by starch or flour, is a condition of being loosely held together without any plan. The molecules have no particular attraction for each other, and any movement or rearrangement they may have will not make any attraction possible because the atoms and groups in the molecules do not attract each other, no matter what their positions may be. On the other hand, in a crystalline solid the molecules are held together in a fairly rigid form because atoms or groups in the molecules do attract each other. This form may be distorted or changed, but this only establishes a new arrangement, and the rigidity still persists. In other words, the molecules of a crystalline substance may be unoriented or they may be oriented in some unidirectional manner. The molecules of a solid substance are not as free to move about as those of a liquid, and their movements are very much more restricted than those of a gas. They do move, but the distances they can move are very short, and the types of movement they can exhibit are mostly rotational and vibrational. The nature of atoms and groups in a molecule determines whether the solid substance will exist normally in the amorphous or crystalline form. In the vinylidene resins there are enough polar groups to cause the normal state to be partially crystalline. This means that if the resin should be made to take on the amorphous state it will gradually change to the crystalline state. X-ray measurements show that the molecules can change position in relation to each other so that the resin becomes partially crystalline. This change takes place because of the attraction between atoms of adjacent molecules, and therefore we should expect the tensile strength of the partially crystallized form to be greater than that of the amorphous form. Since such an increase in strength is brought about by a partial rearrangement of molecules, any agency that would facilitate the rearrangement should hasten the formation of a stronger product. Heat is such an agency because it stimulates movement. Goggins and Lowry[1] showed that the effect of heat on the time of recrystallization is not a straight-line function. This is shown by the figures in Table 53.

Thus, by controlling the temperature of the amorphous resin, its recrystallization can be controlled.

TABLE 53

EFFECT OF HEAT ON RECRYSTALLIZATION OF SARAN

Temperature, ° C	Time of Recrystallization, minutes
10	350
20	80
30	20
40	6
50	2.5
60	1.1
70	0.7

When Saran is first extruded it is a soft, weak, pliable, amorphous material. If left at room temperature, it will harden and then slowly change to a partially crystalline form in which the crystals have an unoriented or random arrangement. With an increase in the proportion of crystallites in the solid its tensile strength goes up, and thus the control of extrusion and subsequent heat treatment permits the production of solid filaments with quite a wide range of properties. For example, the tensile strength can be increased from 4000 lb per sq in. for the unheated, unoriented filaments to 12,000 lb per sq in. for the heated (but still unoriented) filaments.

It has been found that still greater strength can be obtained by further working the material, that is, bringing about crystalline orientation by stretching. Before Saran is extruded, it is heated above its crystallite melting point, in which state it is a liquid and is neither amorphous nor crystalline. It is then extruded and solidified by quenching in water to form a supercooled, completely amorphous solid. It must remain in this condition during the stretching treatment, and so it is drawn out at once, while still supercooled, so that orientation may take place while recrystallization is in progress. Stretching orients the crystallites and arranges the long polymer chains lengthwise of the filament. It also reduces the diameter so that an elongation of 400% makes the filament about half as thick. The application of heat increases the degree of recrystallization (Table 53), but it is the elongation that induces the orientation and determines the final strength. The relation between elongation and strength is shown in Table 54.

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[1] *Ind. Eng. Chem.*, **34**, 327 (1942).

TABLE 54

ELONGATION AND STRENGTH OF SARAN*

Per Cent Stretch, 5 minutes	Tensile Strength, lb per sq in.
0	8,000
50	15,000
100	17,000
150	17,000
200	17,000
250	17,000
300	19,000
350	32,000
400	60,000

* Goggins and Lowry, *Ind. Eng. Chem.*, **34**, 327 (1942).

As a rule, the finer filaments are stronger than the coarser ones; that is, they have a higher unit tensile strength. This is because they are more thoroughly supercooled by the quenching operation. Saran has a low thermal conductivity; when large filaments are quenched they are not supercooled in the center, and some recrystallization starts in that region before they are stretched. As a consequence they cannot be fully oriented and they have somewhat smaller tensile strengths.

Stretching orients the crystallites so that they are lined up along the long axis of the filament. This increases the strength of the filament lengthwise where it is needed in a textile fiber. It is not so necessary that a fiber have a great crosswise strength. This is known as a unidirectional property. Other such properties are elasticity and flexibility.

PROPERTIES OF SARAN MONOFILAMENT

Saran, with a specific gravity of 1.68 to 1.75, is heavier than most fibers. It has good strength (30,000 to 40,000 lb per sq in.) and good elasticity (25 to 30%). It has a high abrasion resistance, so that it will not become fuzzy, and a good flexibility. It will not burn. In addition to its strength, abrasion resistance, and elasticity, other properties that make it suitable for industrial and textile fabric manufacture are its general resistance to chemical reagents, to aging, and to sunlight, and its nonabsorbency of water. Saran is not affected by weak or strong acids or alkalies, nor is it sensitive to the ordinary organic solvents. It is darkened very slightly by direct sunlight but loses no strength by aging. It is weatherproof and insectproof. After immersion in water for 24 hours it is found to have absorbed less than 0.1% water. This means that the wet strength of Saran fabrics will be as great as their dry strength. This is a very desirable property when one considers the many outdoor uses to which fabrics are put and the many indoor uses in which fabrics should retain their strength in the presence of water. However, even though Saran will not absorb water it can be produced in quite a range of colors by incorporating pigments during its manufacture.

The main objection that might be raised against the use of Saran in textiles is its lack of resistance to heat. It should never be heated above 75° C, because above that temperature it will shrink and lose some of its strength, and at 115° C it will start to soften. The effect of heat on the tensile strength of Saran filaments is shown in Table 55.

TABLE 55

EFFECT OF HEAT ON STRENGTH OF SARAN MONOFILAMENT*

(Figures for oriented cordage of 0.027 in. diameter)

Tensile Strength, lb per sq in.	Temperature, ° C
37,500	30
37,150	45
29,000	60
26,000	75
24,500	90
21,000	105
14,000	120

* Goggins and Lowry, *Ind. Eng. Chem.*, **34**, 327 (1942).

If the material is not heated above its softening point, it will regain its original strength when cooled to room temperature. However a filament with Saran's properties will have many uses in which high temperatures are never encountered. If Saran fabrics are eventually manufactured, they can be as carefully protected from high temperatures as Celanese and other cellulose acetate fabrics now are.

USES FOR THE VINYLIDENE FILAMENTS

One of the first uses made of Saran was in the manufacture of industrial filter cloths. Students of chemistry usually think that when a mixture of solid and liquid is to be filtered it is poured onto a folded filter paper in a funnel. However, there are many industries in which hundreds of gallons of such mixtures must be filtered. Some of the liquids in such mixtures are strongly acid or caustic, and the filter material used must withstand the action of such liquids.

Such material must also be strong because industrial filtering is often done under pressure. Various types of cloth have been used, but in many instances they have had to be replaced very frequently, which has caused loss of time and money. Now filter cloths of Saran are found very satisfactory because they are strong enough, are not affected by any acids or alkalies, and are easily cleaned when necessary. It is understood that such filter fabrics cannot be used at high temperatures.

Both Saran and Velon were used in 1942 for transportation cloth, that is, coverings for seats in subways, trains, and buses. They stood up very well, and the Firestone Company again began to manufacture such materials in 1946. Furniture upholstery materials were the next step. Such furniture and seat covers wear very well, can be used out of doors, will resist moths and fungi, and can easily be wiped off with a damp cloth if anything is spilled on them.

These filaments are suitable for sports use, for fish lines and leaders, tennis rackets and nets, shoes, etc. In 1946 Velon and Saran screens for windows and porches became a welcome addition to the consumer market as a substitute for scarce metal screening.

At the present time vinylidene monofilaments are extruded in sizes from 0.005 to 0.05 in. The finest of such filaments would be about seven times as thick as an average American cotton fiber.

Experiments are being conducted on the production of much finer multifilament yarns which may eventually find use in the textile field.

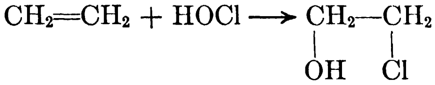
ORLON ACRYLIC FIBER

The du Pont Company is the third large organization to become interested in the possibilities of synthetic polyvinyl resins in the field of textile filaments. They have patented the manufacture, processing, dyeing, and use of resins that are called Orlon acrylic fiber. Orlon resin is made by the addition polymerization of acrylonitrile, $CH_2{=}CH{-}CN$, but the same name may be applied to other resins made by the copolymerization of acrylonitrile with small proportions of other ethylenic compounds.

Acrylonitrile may be made from acetylene or from ethylene. Addition of HCN to acetylene can be effected by means of a barium cyanide-carbon catalyst,

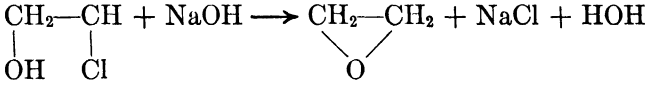
$$HC{\equiv}CH + HCN \longrightarrow CH_2{=}CH{-}CN$$

When ethylene is treated with hypochlorous acid a chlorohydrin is formed,



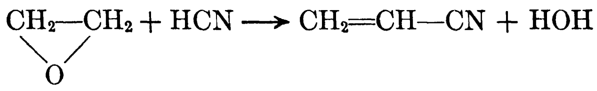
$$CH_2{=}CH_2 + HOCl \longrightarrow \underset{OH}{CH_2}{-}\underset{Cl}{CH_2}$$

which will split off HCl when reacted with NaOH to form ethylene oxide,



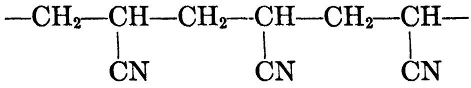
$$\underset{OH}{CH_2}{-}\underset{Cl}{CH} + NaOH \longrightarrow CH_2{-}CH_2\ (\text{bridged by } O) + NaCl + HOH$$

The three-membered ring is easily split by HCN, and the resulting cyanoalcohol is dehydrated to yield acrylonitrile,



$$CH_2{-}CH_2\ (O) + HCN \longrightarrow CH_2{=}CH{-}CN + HOH$$

Acrylonitrile is easily polymerized by peroxide catalysts to form polyacrylonitrile resin, a long-chain linear polymer, a fragment of which may be represented by



$$-CH_2{-}\underset{CN}{CH}{-}CH_2{-}\underset{CN}{CH}{-}CH_2{-}\underset{CN}{CH}-$$

It has been demonstrated that the CN groups do not take part in the polymerization, and yet the polymer does not have the expected properties of an ordinary nitrile.

You will recall that nylon is spun by extruding the molten resin, and that the filament is formed by cooling. This procedure cannot be followed in the manufacture of Orlon because of the higher temperature that would be necessary. Consequently the resin must be dissolved in a suitable solvent and this solution extruded. Considerable research was necessary to discover the proper solvent for this purpose, because of the resistance of Orlon to all ordinary organic solvents; some fairly good solvents were objectionable because of certain operating conditions. Among the solvents that have been found adequate for the preparation of spinning solutions are dimethylformamide, *m*- and *p*-nitro phenols, dimethylmethoxyacetamide, and tetramethylenecyclosulfone.

After extrusion and coagulation, the filaments are oriented and stabilized by stretching. During the period from July 1947 to September 1948, the du Pont Company was granted 24 patents covering all phases of Orlon manufacture. The construction of a 20-acre plant near Camden, S. C., was started in March 1949.

Properties and Uses for Orlon

The properties of a filament like Orlon must be considered from more than one point of view, because of the varied possibilities in its use. We must think of its domestic uses, both indoors and outdoors, and also its applications in industry. We find that Orlon continuous filament is more like silk than any other manufactured textile filament, in that it has the warm, dry, luxurious feel, and the dimensional stability of silk even at high humidities. Orlon staple fiber is said to be more like wool than any other synthetic fiber, owing to its high thermal insulation characteristics, its exceptional bulking property, and its good recovery from wrinkling. It is one of the best textile materials for outdoor use because of its almost perfect resistance to the damaging effect of sunlight and to molds, mildew, and insects, its very low shrinkage, and its high tensile strength, even when wet.

Orlon is especially suitable for industrial fabrics because of its high tenacity (both wet and dry), its dimensional stability (both wet and dry), its low specific gravity, its resistance to strong mineral acids, its fair degree of resistance to alkalies, its rapid-drying quality, and its good abrasion and folding resistance.

Comparison of many of the physical properties of Orlon with other textile fibers will be found in the tables in Chapter 6. Additional characteristics are discussed in the following paragraphs in this chapter. Most of this information is quoted from the initial announcement made to the textile trade by the du Pont Company.[2]

As low density of textile fibers is desirable, it should be noted that Orlon (sp gr = 1.18) is surpassed only by nylon (sp gr = 1.14). Cellulosic fibers are about 28% heavier than Orlon.

Microscopic examination of Orlon acrylic fiber shows that it has a cuticle or skin covering the inner portion (cortex) of the filament. The cortex contains minute air-pockets or vacuoles which do not appear in the cuticle. The most prevalent shape found in cross-sections of this filament is that of a dumbbell (the so-called dog-bone shape), although many cross-sections have a cloverleaf shape.

The tenacity of Orlon ranges from 4.0 to 4.8 denier, which makes it stronger than regular type rayons and about the same as silk, although it is not so strong as regular nylon. One advantage it has, even over the high tenacity rayons, is that it retains over 90% of its strength when wet.

The elongation and elastic properties of Orlon are quite good. The elongation of the dry filament ranges from 16 to 21%, which is not particularly unusual for textile fibers, but the unexpected thing is that the elongation of the wet filaments is the same. Thus cloths made from this filament may be laundered and handled while wet with little danger of distortion. The extent of elongation is not affected by heat up to 175° C.

The elastic recovery of Orlon is about the same as that of nylon and much better than that of the rayons; however, it excels nylon in its resistance to stretch, that is, the amount of stress or load that is required to stretch it, and this is true of the wet filament as well as the dry. For example, the following loads are required to produce an extension of 1.5% in length for the designated filaments:

	Dry, gm/denier	Wet, gm/denier
Orlon	0.8	0.7
Nylon	0.5	0.3
Acetate rayon	0.5	0.4
Viscose rayon	1.3	0.3

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[2] A paper (unpublished) given by Dr. J. B. Quig of the du Pont Company before the American Association of Textile Technologists, December 1948.

From these figures we can draw the conclusion that Orlon will withstand rough handling when wet.

Orlon is outstanding in its low absorption of water and moisture regain, and is in the same class as Saran and Vinyon in this respect. These three filaments will absorb less water than any of the other textile fibers, and the moisture content under any condition of humidity will be lower than that of any of the other fibers. Because of its low moisture absorption, Orlon will dry rapidly after washing.

Fabric	Per Cent of Its Weight Absorbed when Immersed in Water
Orlon	2.5
Nylon	8.0
Acetate rayon	60.0
Viscose rayon	125.0

Fabric	Per Cent of Moisture Regains when Exposed to Atmosphere of 60% R.H. at 70° F
Orlon	0.9
Nylon	3.4
Acetate rayon	5.4
Viscose rayon	12.0

It is well known that the amount of shrinkage a fiber will suffer depends on the shrink-producing medium, the conditions, and the type of fabric construction. Table '56 shows the shrinkage of Orlon yarns (not fabrics) under various conditions, both wet and dry.

TABLE 56

SHRINKAGE OF ORLON YARNS

Medium	Time, minutes	Shrinkage, %
Boiling water	10	1.5
Steam at 117° C	20	1.3
134° C	20	7.5
Hot air at 100° C	30	0.3
125° C	30	2.5
150° C	30	3.6
175° C	30	5.0

Figures of this sort may serve as a guide during the finishing of

Orlon fabrics for dimensional stability. During such finishing operations the fabric should be exposed to temperatures higher than those that will be encountered in use, in order to secure the proper stability.

The following paragraphs show the resistance of Orlon acrylic fiber to agencies that usually damage or destroy textile fibers. These agencies are sunlight, heat, repeated folding or flexing, abrasion, and micro-organisms.

The almost complete resistance of Orlon to the deteriorating action of sunlight is one of its most important properties. Samples of Orlon and cotton were exposed to sunlight in Florida, where the effect of ultraviolet light is very intense, for 385 days. At the end of this time the Orlon cloth had lost about 10% of its strength, and the cotton cloth about 50%. In a test to show the effect of both sunlight and weathering in an industrial area, samples of several textile materials were exposed at Wilmington, Del. These include nylon, silk, viscose rayon, linen, acetate rayon, cotton, Cordura, and Orlon. Over a period of 20 to 48 weeks all the materials except Cordura and Orlon had lost 100% of their strength; Cordura had lost 54%, and Orlon 14%. The strength of Cordura was entirely destroyed after 86 weeks, at which time Orlon had lost only 22% of its strength. It is thus seen that Orlon is extremely well adapted to outdoor use.

Orlon has good resistance to heat. This is illustrated by the accompanying list, which shows how the tenacity of Orlon varies with the temperature at which it is measured. The figures are the percentage change in strength (an increase or decrease) compared with the tenacity when measured at 25° C.

Temperature, °C	Change in Strength, %
−40	+37.5
+25	0
75	−16.5
100	−26.7
125	−33.0
150	−49.0

It is seen that Orlon behaves in the expected manner in that it is weaker at higher temperatures. However, at lower than ordinary temperatures it becomes stronger but at the same time shows no sign of becoming brittle or too rigid.

Exposure to dry hot air affects the strength very little, even after several days. Exposures at 125° C for 32 days caused no loss in strength, that is, when the tenacity was measured each time at 25° C. At 150° C there is a 40% loss after 8 days. There is considerable yellowing of the filaments when so exposed, and a decrease in abrasion resistance; for example, after 16 days at 100° C the abrasion resistance is only about one-third of the initial resistance.

Orlon fiber is destroyed by temperatures that would ordinarily cause a fire, but it does not flash burn. A lighted cigarette, for example, will not cause Orlon fabrics to burn.

The flex life of Orlon is extremely good. It will withstand over 300,000 flexes, whereas wool fails after 44,000, silk after 5000, viscose rayon after 2500, and acetate rayon after 200.

Orlon cannot compete with nylon in resistance to abrasion, but on this score it is better than any of the rayons. Its resistance to micro-organisms and insects is excellent.

Among the chemical properties of Orlon we shall discuss its reactions with strong mineral acids and alkalies, bleach liquor, and solvents.

Orlon should be very satisfactory for making industrial fabrics that may be subjected to the action of strong mineral acids. It shows no loss in strength when immersed in 20% HCl for 49 days and is not affected by concentrated HCl up to 9 days. It will withstand the action of 20% HNO_3 for 56 days, and 40% HNO_3 for 49 days.

The effect of sulfuric acid on Orlon has been studied in some detail. Various concentrations of acid were used at four different temperatures. The filament is not attacked by 60% H_2SO_4 at 25° C even after 64 days. However, at higher temperatures degradation starts in a shorter time, but there could be little objection to its degree of resistance. Orlon shows no loss in strength in 50% H_2SO_4 up to 64 days; at 75° C, deterioration is noticeable in 40% H_2SO_4 after 16 days, and in 30% H_2SO_4 after 64 days. Orlon will withstand the action of 20% H_2SO_4 for 10 days at 100° C, and the action of 8% H_2SO_4 for 16 days at the same temperature. It is evident that Orlon is exceedingly resistant to strong mineral acids, even at high temperatures.

Orlon is not equally resistant to caustic alkalies. Orlon will deteriorate in 10% $NaOH$ after about 16 days at 25° C, but it may be immersed in 2.5% NaOH for 64 days without any harm. At higher temperatures, as would be expected, the fiber is attacked in a shorter length of time; at 50° C it is affected in 8 days by 1.5% NaOH. At still higher temperatures it deteriorates in a matter of hours instead of days; for example, at 75° C, even 3% NaOH will weaken Orlon in about 2 hours. The filament is quite easily soluble in boiling 10% NaOH. Although Orlon is not so resistant to alkalies as to acids, it is still perfectly adequate in boiling-off operations, scouring, and dyeing in alkaline baths.

The chances for damaging Orlon during hypochlorite bleaching are much less than for cotton, acetate rayon, or nylon; in fact, we may consider Orlon very resistant to bleaching agents. It is well known that cotton and rayon are easily damaged by bleaching and suffer an appreciable loss in strength. If these fibers are immersed in a bleach liquor containing 0.1% available chlorine at 77° C (pH = 13), cotton will lose about 40% of its strength in 2 hours; after 3 hours it will have lost 50% of its strength. After such a 3-hour treatment acetate rayon will have lost 35% of its strength, and nylon 20%. The loss in strength for Orlon after such a treatment is only about 9%. Acetate loses all its strength after about 6 hours, and cotton after 8½ hours, but Orlon loses only about 12% of its strength.

Orlon is not soluble in the ordinary organic solvents, but it can be dissolved by concentrated solutions of salts, such as lithium bromide, aluminum perchlorate, and sodium or calcium thiocyanates. It is also soluble in solutions of many quaternary ammonium salts. Among the more usual organic solvents suitable for dissolving polyacrylonitrile are *m*- and *p*-nitrophenol, dimethylformamide, dimethylmethoxyacetamide, and tetramethylenecyclosulfone.

Orlon appears to have varied uses and to fill definite needs. The attributes on which its value for domestic and apparel fabrics may be based are its high strength, its resistance to sunlight, soot, and atmospheric gases, its excellent bulking and covering power, its warm, dry, silklike feel, its easy launderability and durability during laundering, its quick-drying property and dimensional stability, and its resistance to moths and mildew.

In apparel fabrics Orlon can be used in sports clothes, such as bathing suits, jackets, shirts and slacks, in dress shirts and lingerie, and in tricot fabrics. Some of its domestic uses are for curtains, window shades, Venetian blind tapes, raincoats, and umbrella fabrics.

The properties which make Orlon suitable for industrial uses are somewhat different. They include its high strength, its dimensional stability, its resistance to mineral acids and micro-organisms, its low moisture content, low density, and good resistance to heat. It can be used in filter cloths, tents, tarpaulins, sailcloth, awnings, belting, etc.

QUESTIONS

1. What term is applied to the process by which a resin is converted into a plastic? What is usually necessary in order to do this?

2. Explain the difference between condensation polymerization and addition polymerization. Give examples of filaments made from each.

3. What is meant by the polyvinyls and the vinylidenes?

4. What is the objection to the use of polyvinyl chloride or polyvinyl acetate alone for making textile filaments? What is the proportion of the two in Vinyon?

5. How are vinyl chloride and vinyl acetate made? How can they be polymerized to form resins?

6. Tell briefly how Vinyon is manufactured.

7. Give the properties of and uses for Vinyon.

8. How is vinylidene chloride made? How can it be polymerized?

9. With what is vinylidene chloride copolymerized to make Saran? Show the joining of two molecules of each.

10. Name some outstanding properties of Vinyon and Saran and the specific uses which these properties fit them for.

11. Describe the formation of a Saran monofilament. How can it be made stronger?

12. What are the limitations on the heating of Vinyon and Saran?

13. What uses are made of these two filaments?

14. State the process of making the resin Orlon acrylic fiber.

15. How is it possible to have more than one type of Orlon?

16. Show how acrylonitrile can be made.

17. Describe the microscopic appearance of Orlon.

18. Compare the behavior of Orlon with nylon and rayon when treated with strong mineral acids, caustic alkalies, and bleach liquor.

19. How does Orlon compare with other fibers in its resistance to sunlight, abrasion, and micro-organisms?

20. How does Orlon compare with other fibers in tenacity, elongation, and specific gravity?

21. For what purposes can Orlon be used?

13 · Man-Made Protein Fibers

These new fibers cannot be considered synthetic because they are not built up in the laboratory or plant. It is true that they were made and developed in a laboratory, but the process was simply one of treating and modifying certain naturally occurring raw materials, and not by reacting chemical substances to make a new material. The principle involved in the manufacture of a protein fiber is simple. Theoretically, any protein-containing substance may serve as a starting material, and the protein may be extracted from it, dissolved in a suitable solvent, and extruded into a coagulating bath according to the techniques of rayon manufacture. Many proteins have been investigated, but only four have shown possibilities of being commercially important. They are milk casein, the zein of corn, and the proteins of soybean and peanuts.

The first man-made protein fiber was discovered, patented, and developed in Italy in 1935 by Ferritti, who used the casein of skim milk as the raw material. This casein fiber was manufactured in Italy under the name Lanital, in Holland as Casolana and Lactofil, in Germany as Tiolan and Thiozell, in England as Fibrolane, and in the United States as Aralac.

Casein fiber is made by extracting the casein from skim milk, dissolving it in dilute alkali, and extruding it into an acid coagulating bath, where it is hardened and cross-linked with formaldehyde.[1]

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[1] Readers who may be interested in the details of casein fiber are referred to:
Whittier and Gould, *Ind. Eng. Chem.*, **32**, 906 (1940).
Carpenter and Lovelace, *Ind. Eng. Chem.*, **34**, 759 (1942).
Sherman and Sherman, *The New Fibers*, D. Van Nostrand Company, 1946, Chapter 9.

Zein Fiber: Vicara

The second commercially successful man-made protein fiber was produced from the vegetable protein zein, which is contained in corn gluten. Mr. L. C. Swallen of the Corn Products Refining Company applied for a patent[2] in 1935 for the manufacture of such a fiber. Much of the fundamental research in connection with the use of zein for fiber production has been done at the Northern Regional Laboratory of the U.S. Department of Agriculture at Peoria, Ill., and also the Harris Research Laboratories in Washington, D.C. Industrial research and development were carried out over a period of years by W. P. ter Horst of the Virginia Carolina Chemical Corporation, with the result that this company in 1948 was in commercial production of a zein fiber called Vicara, at the former Aralac plant in Taftville, Conn. Vicara was the only man-made protein fiber being manufactured in the United States in 1949.

The raw material from which Vicara is made is zein, a high-polymer protein with a molecular weight of about 40,000. It belongs to the class of proteins known as prolamines, that is, proteins which are insoluble in water but soluble in alcohols; in fact, zein is separated from the gluten of corn by treatment with isopropyl alcohol. On the other hand, it resembles the casein of skim milk in that it can be dissolved by dilute alkali. We should expect a fiber made from such a raw material to have similar properties, but we shall find that the properties of Vicara differ greatly from those of zein. This, of course, is due to changes imposed upon the original protein during the manufacture of the fiber. These changes can be varied to such an extent that Vicara may be considered a tailor-made fiber; for example, one type of Vicara can be blended with wool, cotton, silk, or rayon for making domestic apparel fabrics, whereas another type can be blended with fur to make felt hats. This latter type is known as V.C. Fiber-H, or Zycon, but in this book we are discussing only textile fabrics. Much of the information given here was furnished by the Virginia Carolina Chemical Corporation of Taftville, Conn.

THE MANUFACTURE OF VICARA

Many phases of the manufacture of Vicara fiber from zein cannot be discussed in detail, because such factors as time, temperature, concentrations, tension, stretch, etc., are the subjects of patents applied for but not yet issued. However, we shall be able to get a fairly good picture of the procedures and the results obtained by each.

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[2] U.S. Patent 2,156,929 (1939).

The procedures in the manufacture of Vicara are in general like those for rayon. These consist of extruding a solution through a spinneret into a coagulating bath, followed by suitable after-treatments. Thus the three main steps in making Vicara are (*a*) the preparation of a suitable spinning solution, (*b*) extrusion and coagulation, and (*c*) after-treatments.

Croston, Evans, and Smith[3] investigated the preparation of the spinning solution. It is found that a high-viscosity solution containing 13 to 16% zein is required, and that this can be obtained in solutions of NaOH having a *p*H of 11.3 to 12.7. The viscosity of such a solution is so high that it is almost at the gel stage; that is, if the mass is cut, it will slowly fold back together again. One important factor in attaining this high viscosity is the matter of time. Spinning solutions are always aged before they are extruded.

Such a viscous solution of zein could be used for extrusion, but it is found that the addition of some other substances gives better results. The presence of a small amount of formaldehyde will give a little added strength to the filaments as they are being coagulated; the addition of denaturing agents, such as urea or alcohols, will decrease the time required for aging. The final fiber seems to be softer if urea is included in the spinning solution.

To prepare a typical spinning solution, one can wet out the dry powdered zein with water until a smooth suspension is obtained. Zein is 12% and the water is 88% of the total solution. Then a 0.4 *N* NaOH solution (1.7%) containing 0.5% formaldehyde and 1.5% urea is stirred in slowly. This solution is then aged until it has the proper viscosity.

When the spinning solution has been properly aged, it is forced through a large spinneret under pressure. The spinneret is entirely different from that used for making filament rayon. Vicara is put on the market as staple fiber in lengths of 0.5 to 6 in., and for this reason large spinnerets with thousands of openings are used, thus producing a large mass of filaments called tow. This tow may have as many as 250,000 filaments in it.

[3] *Ind. Eng. Chem.*, **37**, 1194 (1945).

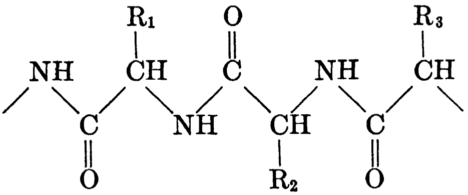
The precipitating bath must be acid in order to coagulate the protein from the alkaline solution, but only dilute acid baths are necessary, as the spinning solution does not have high concentration of alkali. It has been found that the addition of certain salts to the coagulating bath will speed up coagulation, thus giving the filaments a surface which keeps them from sticking together. A typical coagulating bath may contain 4.7% H_2SO_4, 3.1% CH_3COOH, and 4.4% $ZnSO_4$. Streams of protein solution enter this bath, coagulation takes place, and the filaments are gathered together to make the tow, which is then wound on a reel while it is washed with large amounts of water to free it from acids and salts.

The tow at this stage is entirely unsuitable for textile uses and must be given various after-treatments for the purpose of producing the best possible fiber for a particular use. This is where the tailoring of the fiber is done. It is possible to regulate the strength of the fiber, to make it water-absorbent or water-repellent, to make it very soft or harsher, etc. When the fiber is coagulated the protein molecules are arranged at random, and this arrangement contributes to the weakness of the filaments. The research of Carothers showed that stretching will bring about an orientation of molecules in an aligned manner, and so one of the most important after-treatments will be orientation by stretching. However, the tow is not quite hard enough to be handled in the stretching operation, and it must be given a precure treatment with formaldehyde before stretching. After stretching it is given a postcure treatment.

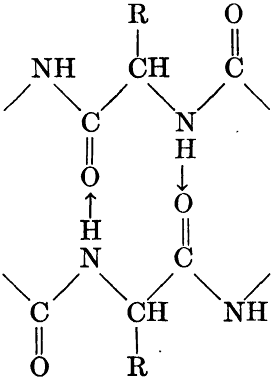
Before looking at the effect of formaldehyde, let us see how adjacent or parallel chains of protein molecules are held together. It is thought that they are held because of the existence of hydrogen bonds, as illustrated by

$$\mathrm{C::O + H:\overset{|}{N}— \longrightarrow C::O:H:\overset{|}{N}—}$$

The strong attraction of hydrogen for electrons makes possible a union in which hydrogen atoms can vibrate between oxygen and nitrogen. It is not inferred that the hydrogen has a valence of 2, but that the formula shown above represents a resonating system or structure in which the oxygen and nitrogen are held together by means of a hydrogen bond or bridge. Recall that the skeleton of a protein molecule can be represented by this general formula:



If two such chains lie side by side, the NH group of one chain might be joined to the CO of the other chain by means of a hydrogen bond. This is shown in the following fragments, where the arrows represent hydrogen bonds.



Although such hydrogen bonds have considerable strength, real primary valence cross-linkages would be still stronger. These can be achieved with formaldehyde. The hardening of proteins by means of formaldehyde has been practiced for a long time and has been the subject of much discussion in textile chemistry literature. Some of the most recent and reasonable suggestions regarding the mechanism of this reaction have been made by Carpenter and Lovelace.[4] They suggest that added strength results from the formation of cross-linkages between adjacent peptide chains due to the reaction between HCHO and the hydroxyl groups of the protein. Obviously if chains of amino acid fragments are prevented from slipping past each other by binding them together with cross-linkages, the strength of the material will be increased. If the formation of these cross-linkages involves hydroxyl groups, these groups will be eliminated or blocked. There seems to be some connection between OH groups in fibers and their capacity for absorbing water. The fewer OH groups present, the less will be the absorption, and therefore, if OH groups are blocked by the action of some reagent, the resistance to water absorption will be increased.

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[4] *Ind. Eng. Chem.*, **34**, 759 (1942).

One of the well-known reactions between formaldehyde and alcohols is the formation of acetals (diethers) as shown by

$$\text{X—CH}_2\text{OH} + \text{H}_2\text{C=O} + \text{HOCH}_2\text{—X} \longrightarrow \text{X—CH}_2\text{—O—CH}_2\text{—O—CH}_2\text{—X} + \text{H}_2\text{O}$$

The alcohol hydrogens from two molecules of alcohol combine with the carbonyl oxygen of formaldehyde to form water, and the organic residues combine to form a diether (an acetal). If the CH_2OH groups in the above equation are a part of adjacent peptide chains in a protein, it is seen that these two chains are joined together by a methylene group (CH_2). Thus when Vicara tow is treated with formaldehyde some of the parallel peptide chains are bound together, and the filaments will be strengthened to an extent proportional to the number of cross-linkages introduced.

Vicara tow is precured by a mild treatment with formaldehyde preceding the stretching operation. The concentration of formaldehyde, time of immersion, and temperature are factors which determine the amount of stretch given the tow and also some of the properties of the final fibers. A low cure results in greatly elongated filaments which will yield flexible, small-diameter fibers susceptible to a large amount of shrinkage in water. A high cure yields filaments which cannot be stretched so much, but after stretching they are much stronger than the low-cured fibers; however, they are coarser and stiffer. Excessive curing results in brittle fibers. The tow is usually stretched from 200 to 250% in length at a temperature of 45 to 60° C.

The fiber may also be given an acetylating treatment after stretching, because such a treatment will endow the filaments with desirable properties. If zein fiber is treated with an acetylating agent such as acetic anhydride, the hydrogens of residual NH_2 groups and OH groups of amino acids such as tyrosine can be replaced with acetyl groups according to the following type of reaction:

$$\text{X—OH} + (\text{CH}_3\text{COO})_2\text{O} \longrightarrow \text{X—O—CO—CH}_3 + \text{CH}_3\text{COOH}$$

This treatment would be applied after the filaments have been coagulated, precured, and stretched, and therefore it is one in which the surface of the filament is modified. If the surface is changed by acetylation, the fibers will have different physical and chemical properties than unacetylated fibers.

Evans, Croston, and Etten[5] made a complete study of the acetylation of zein fibers, and much of the following discussion is based on their work. They found that acetylation improves the wet strength of zein fiber, gives it a much greater resistance to boiling water, decreases its water-absorbing capacity, makes it whiter, and improves its softness by moderating the severe formaldehyde postcure.

The acetylating agent is acetic anhydride containing 5 to 10% acetic acid, with sodium acetate or sulfuric acid as a catalyst; for example, during a 20-minute treatment without catalyst the product will contain 1.7% acetyl groups, whereas with 1% sodium acetate, or 0.1% H_2SO_4, about 5% acetyl groups are combined in the same length of time. Larger amounts of H_2SO_4 must be avoided because of its weakening action on the ultimate fibers. It is found that the extent of acetylation can be controlled by varying such factors as concentration, time, and temperature.

It has been said that acetylation will increase the strength of zein fiber, but the filaments must be stretched before this increase can be attained. The difficulty is that if the filaments are subsequently immersed in hot water they will shrink back to the original length. This is where the postcure plays its part. If the tow, after acetylation, is stretched and held under tension while it is treated with formaldehyde, new cross-linkages will be introduced; thereafter the fiber will shrink comparatively little, even in boiling dilute alkali for 2 hours.

In a typical procedure the dry tow, after being precured so as to contain about 1% formaldehyde, and then stretched, is immersed in the acetylating mixture (acetic anhydride, acetic acid, and catalyst) for the proper length of time. During this immersion the filaments swell considerably and shrink as much as 50%. They are then withdrawn, washed thoroughly on drums, and stretched 100 to 150%. The postcure treatment is given while they are under tension. This consists of immersion in about 10% formaldehyde at 60° C for 15 to 45 minutes, at $p\mathrm{H}$ =

[5] *Textile Research J.*, **17**, 562 (1947).

1. This cure is catalyzed by salts such as $(NH_4)_2SO_4$ or NH_4Cl with addition of the corresponding acid so as to give the proper *p*H. The tow is finally washed well and dried. The final content of formaldehyde is 3.5 to 4.0%.

When acetylated fibers are treated with dilute alkali ($pH = 8$), about 30% of the acetyl groups are removed in 30 minutes. Unacetylated fibers will give a dark red color with Millon's reagent, but acetylated fibers give a very weak color; however, after alkali treatment the color is much stronger.

After Vicara is completely treated it is cut into staple lengths of 0.5 to 6 in. The denier is from 2 to 4.

PROPERTIES OF VICARA

It must be understood that Vicara is not a substitute for any other known fiber, nor should it be considered as an impurity if blended with other fibers in a yarn. It has some properties which are regular and to be expected, but it also has some unique properties, which make it very desirable as a blending fiber. It must be understood, too, that Vicara is a man-made protein fiber, and therefore its properties and potential uses should be compared with those of other man-made protein fibers.

The tenacity of Vicara is not high, and like many other fibers Vicara loses much of its strength when wet. Under ordinary conditions of temperature and humidity, the tenacity is 1.2 gm/denier, which means that it is about the equal of wool. Its wet tenacity is 0.6 gm/denier.

One of the outstanding properties of Vicara is its very good elongation and excellent elastic recovery. When dry it can be stretched about 40% before it breaks, and when wet the elongation is 50%. Its elastic recovery after being stretched up to 5% of its length is practically 100%. This is true even when the fiber is wet. The combination of the two properties of elongation and elastic recovery means that it will be soft and flexible and yet have good dimensional stability, so that it is very suitable for knit goods.

Vicara will not felt as wool does. This is of course highly desirable for many uses, but for cloths which are to be purposely felted it is not advantageous. The properties we have mentioned thus far would indicate that Vicara could be washed and laundered without difficulty. Its launderability is demonstrated by the fact that a test cloth can be laundered five times at the boiling point and show less than 2.5% shrinkage in both warp and filling. It may be boiled in water for many hours without being damaged.

It has an excellent resistance to heat and will not be affected by dry heat up to 150° C, even over long periods of time. At higher temperatures it becomes brittle, and it starts to melt at about 250° C. It burns like wool, but a little more rapidly.

The specific gravity of Vicara is 1.25, which places it about midway between wool and silk. The water absorbency of Vicara is about the same as that of wool; at 65% R.H. at 70° F, the moisture regain is 13%. It swells slightly when immersed in warm water. It has quite good water repellency at ordinary temperatures, but this is lost at temperatures above about 60° C and then regained after drying. This is a very unusual fiber property, and quite desirable, because the inherent water repellency does not interfere with various wet-processing operations, such as scouring and dyeing. This water repellency is permanent at room temperature and is not removed by repeated launderings or dry cleaning. Vicara is not attacked by moths or carpet beetle larvae and is highly resistant to mildew.

Since Vicara is made from a vegetable protein, zein, we should expect it to exhibit chemical properties similar to those of other protein fibers, such as wool and silk. The amino acid composition of zein hydrolysates will be found on pages 46 to 48. It will be noted that the zein amino acids differ from those obtained from wool and silk in three ways. The zein hydrolysate is exceptionally high in glutamic acid (a dicarboxylic acid) and in leucine, whereas the content of lysine (a diamino acid) and of glycine is negligible. Furthermore, zein has a much lower cystine content than wool.

The behavior of Vicara with organic solvents is very interesting, because it is not soluble in any of them. The original raw material, zein, being a prolamine, is soluble in alcohols such as isopropyl alcohol and other solvents, but this characteristic is absent in Vicara; it is not soluble in alcohols, ketones, phenol, acetic acid, hydrocarbons, or any of the ordinary solvents. Thus Vicara can be dry cleaned with safety.

The great resistance of Vicara to the action of mineral acids is unexpected. We know that silk is easily dissolved by concentrated hydrochloric acid and that wool is destroyed by strong sulfuric acid, but Vicara is not appreciably affected by concentrated hydrochloric acid or 70% sulfuric acid. Therefore it is possible to subject Vicara blends to any acid wet-processing treatment.

Vicara is even less sensitive to the action of alkalies and is resistant enough to permit the use of any of the ordinary alkaline treatments. Only about 1% of Vicara fiber is dissolved after a half-hour treatment with sodium hydroxide up to 25% at 50° C.

The high resistance of Vicara to the action of acids and alkalies indicates that it can be blended with wool or cotton and dyed in either acid or alkaline baths, and that it should not be damaged by such operations as carbonizing or mercerizing.

USES OF VICARA

Vicara can be blended with wool to increase the drape quality and softness of the wool without decreasing its warmth. Vicara will also increase wrinkling resistance, so that fabrics will not wrinkle or crease easily. When blended with cotton the draping quality, softness, and elasticity are improved, and when blended with nylon increased absorbency and softness result.

These properties and performance in finished goods make Vicara useful primarily for the following types of textile materials: men's suitings; women's dress goods and suitings; knit goods; infants' wear; sports clothes; hosiery; and upholstery.

Soybean Fiber

There is another vegetable product which can furnish protein. This is the soybean. In 1943 the United States produced more than 200,000,000 bushels of soybeans, which makes this the third largest cash crop in the country. The soybean contains about 35% of a vegetable protein, and because of its increasing production it offers the cheapest and most abundant source of vegetable protein in the world.

The Japanese were among the first to investigate the use of soybean protein in the manufacture of protein fibers, and patents were granted in this country in 1940 and 1941.[6] During 1942 to 1945 several patents issued to Huppert[7] were assigned to the Glidden Company. In 1937 the Ford Motor Company became interested in new commercial uses for soybean, and R. A. Boyer was put in charge of soybean research and development. Two basic patents[8] granted Boyer in 1945 covered the manufacture of soybean fiber. Later Mr. Boyer, with the full and willing consent of the Ford Company, transferred his interests and researches to the Drackett Company in Cincinnati, where he became director of scientific research.

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[6] U.S. Patents 2,192,194, 2,198,538, and 2,237,832.

[7] U.S. Patents 2,298,127, 2,309,113, 2,364,035, and 2,377,885.

There are five main steps in the production of a textile fiber from the soybean: (1) the extraction of oil to obtain an oil-free meal, (2) the extraction of protein from the meal, (3) the preparation of a spinning solution, (4) the extrusion procedure, and (5) after-treatments.

To extract the oil the beans are crushed and then steeped in hexane, which dissolves the oil. The hexane solution is drawn off, and the meal is washed with more hexane to remove residual oil. The oil-free meal is then passed through steam-heated pipes for the purpose of vaporizing the remainder of the solvent.

The separation of the vegetable protein from soybean meal is accomplished by steeping the meal in a 0.1% solution of sodium sulfite for one-half hour. The protein is dissolved by this treatment, and after the mixture has been filtered or centrifuged the protein is precipitated by means of acid. Sulfuric acid is added until the *p*H of the solution reaches 4.5. This is near the isoelectric point of soybean protein, which means that the protein is under conditions of its minimum solubility and therefore will be precipitated. Tanks and other equipment for dissolving and precipitating the protein must be made of stainless steel or lined with glass because soybean protein is discolored by iron.

The spinning solution is prepared by dissolving the protein in an alkaline solution and then allowing it to age until the proper consistency is obtained. Most proteins will gel when the concentration of the solution is above about 12%, but it has been found possible, by special controls in handling the material, to obtain solutions of soybean protein containing as much as 20% solids. The solution is filtered and deaerated by means of a vacuum so as to remove all undissolved particles and air bubbles, and it is then allowed to age at the optimum temperature. During the aging period, the solution becomes more viscous and develops the proper stringiness for spinning.

The spinning operation consists of forcing the spinning solution through a spinneret containing several hundred openings. The fine streams of solution are passed into an acid coagulating bath in which the protein is precipitated as a filament. This precipitating bath is similar to that used in making Vicara. It contains sulfuric acid, which destroys the alkalinity of the spinning solution and precipitates the protein; formaldehyde in the bath acts as a hardening agent; and certain salts, such as sodium chloride or aluminum sulfate, act as dehydrating agents. If the filaments were allowed to dry in this coagulated form they would be weak, brittle, and have little resilience. However, it is found that they can be made stronger and more elastic by a stretching orientation procedure. As in the manufacture of other synthetic fibers, the mass of filaments is picked up by a glass spool or bobbin and passed through the spinning bath to a second spool, which is turning at a higher speed. This causes a stretching of the soybean filaments while they are still in the coagulating bath and brings about a rearrangement of the molecules so as to give the filaments more strength and elasticity.

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[8] U.S. Patents 2,377,853, 2,377,854.

After-treatments of the filaments comprise a hardening treatment, washing, drying, and cutting into the desired staple length. The hardening is done by immersing the filaments in a dilute solution of formaldehyde. The action of formaldehyde on proteins has already been discussed (see page 363).

Soybean fiber varies from white to light tan; it has medium luster and a warm soft feel due to its good resilience. It has a natural crimp with as many as twelve waves per inch, and when mixed with other fibers it can be felted fairly well. It is being extruded in sizes ranging from 3 to 12 denier, and is cut into staple fiber from 0.5 to 6 in. in ¼-in. graduations. The tenacity of soybean fiber is 0.8 to 1.0 gm/denier, which makes it about 80% as strong as wool, but it loses much of this strength when it is wet. Its dry elongation is about 40% and its wet elongation about 60%, both of which figures are higher than those for wool. More recent improvements have resulted in a fiber that resists carbonizing quite well, is not as sensitive to hot alkali as wool is, and can be dry cleaned without damage. Soybean fiber has a density of 1.3, which classes it along with wool, Vinyon, and Vicara. The usual moisture content is from 10 to 13%, and it does not wet as easily as Vicara or wool. It can be dyed with the ordinary acid and chrome dyes usually applied to wool.

It is to be clearly understood that the properties stated are those of the fiber being made on a small scale in 1946. Many of the properties are being improved as the present research program progresses.

It is too early to predict how this new protein fiber will be used, but it should find a good market for blending with other fibers in the manufacture of women's wear and upholstery.

QUESTIONS

1. How do the physical properties of the man-made protein fibers differ from those of the natural protein fibers? What is the probable cause of the low strength of the man-made ones?
2. Who, and in what year, made the first practical and commercially successful casein fiber?
3. What three proteins are mainly used for making the man-made protein fibers?
4. What organization controls the manufacture of Vicara?
5. From what is Vicara made?
6. How is the spinning bath prepared in the production of Vicara? What chemical compounds may be used in it?
7. What type of chemical is used in the Vicara precipitating or coagulating bath?
8. What chemical is used to put cross-links in zein fiber? Does this make it stiffer?
9. How does the extrusion apparatus for making Vicara differ from the usual rayon spinnerets?
10. Is zein fiber made in long filaments like rayon or in short staple like cotton and wool? Why is it made in this particular way?
11. What is the acetylation treatment given protein fibers? What happens to the alcoholic OH groups during this treatment? In what ways does this improve the fiber?
12. After zein fiber is coagulated and is in the form of tow, what after-treatments is it given? What is accomplished by each?
13. Compare Vicara with wool as to wet and dry strength, elongation, elastic recovery, warmth, burning test, and stability toward heat.
14. Discuss the uses for Vicara. Is it generally used alone or blended with other fibers?
15. Outline the steps in the production of a textile fiber from the soybean.
16. How is the vegetable protein separated from oil-free soybean meal?
17. How are spinning solutions prepared for spinning soybean fiber? Is the fiber extruded like Vicara or rayon?
18. What after-treatments is the soybean fiber given?
19. Compare soybean fiber with wool as to wet and dry strength, elongation, moisture regain, and specific gravity.

Glossary

Acele. An acetate rayon (du Pont).

Acetate Rayon. Cellulose acetate regenerated from acetone solutions.

Acetylation. The reaction by which an alcohol or amine is treated with an acetylating agent so as to substitute an acetyl group for hydrogen.

Acetyl Group. The CH_3—CO— group.

Acid Anhydride. A compound which will yield an acid when treated with water.

Acid Dye. Salt of a color acid, from which the color acid is liberated when treated with a mineral acid. Acid dyes are applied to wool from sulfuric acid baths.

Acid Hydrolysis. A degradation reaction brought about by the action (either hot or cold) of acids on such compounds as esters, amides, glycosides, proteins, carbohydrates.

Acylating Agent. Any reagent, containing an acyl group, which will replace a hydrogen of an alcohol or amine, e.g., acid chlorides or acid anhydrides.

Acylation. A type of reaction in which a hydrogen of an alcohol or an amine is substituted by an acyl group.

Acyl Group. The R—CO— group.

Addition Polymer. The product formed by the simple polymerization of a compound, in which molecules add to each other to form rings or long chains, without any other compound being formed by any splitting-off reaction.

Alcoholate. A salt of an alcohol, ROMe, where Me is a metal.

Alkaline Hydrolysis. *See* Acid Hydrolysis. This is the same reaction except that it takes place in alkaline medium.

Alkyl Group. A group of carbons and hydrogens having the general formula C_nH_{2n+1}, with a valence of 1.

Amino Acid. Unless qualified by some specific statement, an organic acid having an NH_2 group on the α-carbon atom.

Amino Group. The NH_2 group found in many organic nitrogenous compounds.

Amorphous Substance. One that exists in a powdery, non-crystalline form.

Amphoteric. Both basic and acidic.

Angstrom Unit. A measure of length equal to 0.0000001 mm or to 1×10^{-7} mm. Abbrev. Å.

Anhydroglucose Unit. A fragment of polysaccharoses which is repeated in the long high-polymer chain. It is equivalent to the pyranose glucose ring minus a molecule of water.

Anion Exchangers. Substances, used in the demineralization of water, which remove acids formed by cation exchangers.

Appendage Fibers. Hair fiber growing on the bodies of animals.

Aralac. A former American casein fiber.

Aryl. A syllable indicating an aromatic grouping of some sort.

Ash. The mineral matter left after a substance has been burned.

Auricon. A crimped staple fiber rayon (American Viscose Corp.).

Avisco. A high-tenacity staple fiber rayon (American Viscose Corp.).

Barbadense. A species of Gossypium (cotton) cultivated in Egypt, Peru, and the West Indies.

Base Exchange Softening. A method for softening water in which the soap-precipitating cations of hard water are exchanged for nonsoap-precipitating ions.

Basic Dye. A salt of a color base, usually applied from neutral or very weakly acid baths.

Bast Soap. Soap liquors left after the degumming of raw silk.

Battage Method. A beating and foaming method for reclaiming wool grease from waste wool scouring baths.

Belastraw. A viscose rayon (Hartford Rayon Corp.).

Bemberg. A cuprammonium rayon (American Bemberg Corp.).

Blending. A term applied to the mixing of different kinds of fibers, which may be carded (or combed) and spun into a yarn of mixed fibers.

Boiling-off. The process by which the silk gum is partially or completely removed from raw silk.

Boiling Out. The process by which cotton is prepared for bleaching.

Bone-dry Weight. The weight of any substance that contains no hygroscopic moisture.

Bourette Silk. A waste silk obtained during the making of schappe silk. It is carded and spun like woolen yarn.

Briglo. A viscose rayon (American Enka Corp.).

Builder. A weakly alkaline substance added to a soap to increase its general detergency.

Butter of Tin. Stannic chloride.

Carbinol. For the purpose of naming, many alcohols are considered as derivatives of carbinol, Ch_3OH, in which one or more of the hydrogens have been replaced by alkyl groups.

Carbonyl Group. The C═O group, which is the functional group of aldehydes and ketones.

Carboxyl Group. The —COOH group, which is the functional group of all organic carboxylic acids.

Carboxylic Acid. Organic acids containing the carboxyl group (—COOH), as distinguished from sulfonic acids, mineral acids, etc.

Cargan. A Belgian casein fiber.

Casolana. A Dutch casein fiber.

Catalyst. A substance that may cause a chemical reaction to take place more easily, faster, or more nearly to completion.

Cation Exchanger. A substance, used in the demineralization of water, which will take out soap-destroying cations and replace them with hydrogen.

Caustic Alkali. Hydroxide alkali, NaOH and KOH.

Celairese. A staple fiber acetate rayon (Celanese Corp.).

Celanese. Acetate rayon (Celanese Corp.).

Chalkelle. A viscose rayon (American Viscose Corp.).

Chlorination. A type of reaction in which chlorine is substituted for hydrogens in a compound, or a reaction in which a compound is treated with a substance capable of yielding chlorine or its equivalent.

Cold Drawing. A stretching operation in which molecules of a high polymer, arranged at random, are orientated.

Combined Alkalinity. Alkalinity that is not free but combined in a compound from which it may be liberated by hydrolysis.

Condensation. Any reaction that occurs with the formation of new bonds between atoms not already joined, and proceeds with the elimination of elements (H_2, N_2, etc.) or simple molecules (HOH, NH_3, ROH, etc.).

Condensation Polymer. A polymer formed by the condensation of two or more molecules of compounds, followed by the elimination of water, ammonia, halogen acid, etc.

Conditioned Weight. The weight of any textile material, consisting of the bone-dry weight plus a standard regain.

Conjugated Double Bonds. An arrangement of bonds such that two double bonds are separated by a single bond.

Copolymer. A polymer produced by the union of two different molecules to form more or less long chains.

Copperas. Ferrous sulfate.

Copper Number. The number of grams of copper reduced by 100 gm cellulosic material from Fehling's solution, or a modification of it.

Copper Silk. Cuprammonium rayon.

Cordura. A high-tenacity viscose rayon (du Pont).

Cortex. The main fibrous part of wool. It is covered by the epidermis.

Corticular Cells. The spindle-shaped cells of the cortex of wool fibers.

Count of Yarns. A number that designates the size of a yarn.

Covalent Bond. A bond between chemical elements in which electrons are shared, the pairs of electrons operating in the outer shells of both elements. The true chemical bond.

Cream of Tartar. Potassium hydrogen tartrate, $KHC_4H_4O_6$.

Crown. A viscose rayon (American Viscose Corp.).

Crystal Lattice. The definite and regular arrangement of the ions in a solid crystalline electrolyte.

Crystalline. A term that describes a substance the component parts of which are oriented or arranged in some definite manner.

Cuprammonium. (1) Another name for Schweitzer's reagent. (2) A type of rayon made of cellulose regenerated from Schweitzer's reagent.

Cuprate Silk. Cuprammonium rayon.

Cuticle. *See* Epidermis.

Decarboxylation. A reaction by which a carboxyl group is split off from a compound.

Degraded Cellulose. Cellulose that has shortened polymeric chains due to either oxidative or hydrolytic action.

Degumming. Same as boiling-off.

Demineralized Water. Water treated to remove all mineral cations and anions. It is the same as distilled water.

Denier. A measure of the weight or size of yarns or filaments in the silk, rayon, and nylon trade. If a filament is a 1 denier filament, 9000 m of it weighs 1 gm. If a yarn is a 30 denier yarn, 9000 m of it will weigh 30 gm.

Dicarboxylic Acid. An organic acid with two acid hydrogens (two COOH groups).

Dispersed Phase. That part of an emulsion which is present in the smaller amount and is dispersed throughout the larger volume of the other component.

Dispersion Medium. The medium in which a dispersed phase is distributed.

D. P. Degree of polymerization.

Dreft. One of the Gardinols.

Dulesco. A viscose rayon (American Viscose Corp.).

Dul-tone. A viscose rayon (Industrial Rayon Corp.).

ELASTICITY. That property of a body by virtue of which it tends to recover its original size and shape after deformation.

ELASTIC RECOVERY. *See* TRUE ELASTICITY.

ELECTROVALENT BOND. A bond between chemical elements formed by the complete transfer of electrons from one atom to another. A salt bond.

ELONGATION. The percentage of length to which a fibrous substance can be extended before it breaks; its percentage of stretch at the breaking point.

EMULSIFYING AGENT. A compound used to increase the ease of formation and the stability of emulsions.

EMULSION. A dispersion of one nonmiscible phase in another.

ENGLO. A viscose rayon (American Enka Corp.).

EPIDERMIS. The outermost layer of a wool fiber. The cuticle or cuticular layer.

EQUIVALENT WEIGHT. That weight of a chemical compound which will release or react with one atom of hydrogen (or its equivalent).

ESTER. A derivative of an acid in which the acid hydrogen has been replaced by an alkyl group or some other organic radical.

ETHER LINKAGE. The —C—O—C— linkage.

ETHYLENIC DOUBLE BOND. Double bonds between carbon atoms such as are found in ethylene.

EXTRACT WOOL. Wool reclaimed by carbonizing mixed goods.

EXTRUSION. An operation by which a mass of molten solid material or solution is forced through fine openings to form filaments.

FAT. A naturally occurring substance with a general formula, $(RCOO)_3C_3H_5$, in which R is a long chain of carbon atoms. A glyceride of high-molecular-weight fatty acids.

FATTY ACID. An acid belonging to the acetic acid family, with the formula RCOOH.

FELTING. (1) A property of wool by which wool cloths can be compacted and made more solid at the time the wool is shrunk. (2) The mill operation by which wool is felted.

FIBRO. A staple fiber rayon (American Viscose Corp.).

FIBROIN. The water-insoluble fibrous protein of silk.

FIBROLANE. A British casein fiber.

FILATURE. A mill in which silk is reeled.

FLOCKS. Very short bits of wool waste.

FORTISAN. A high-tenacity acetate rayon. Saponified acetate (Celanese Corp.).

FREE ALKALI. A term used in soap analysis to designate that alkalinity which is not real soap.

Fulling. A mill operation by which woolen cloths are felted.

Functional Group. That fragment of a chemical compound which, by its reaction, gives to the compound its characteristic chemical properties.

Gardinol. A name applied to a group of nonsoap detergents which are high-molecular-weight alcohol sulfates.

Glanzstoff. A commercial name for cuprammonium rayon.

Glauber's Salt. Commercial crystalline sodium sulfate.

Glyceryl Radical. The $\underset{|}{CH_2}—\underset{|}{CH}—\underset{|}{CH_2}$ group which is found in fats and oils.

Glycoside. A naturally occurring substance which can be split (by hydrolysis) into a simple sugar and some other organic compound.

Gossypium Hirsutum. The botanical species producing the ordinary American upland cotton.

Greensand. A natural zeolite used in the base exchange method for softening water.

Green Vitriol. Ferrous sulfate.

Grege. A thread of reeled silk.

Greige Goods (as the finisher gets them). Cotton goods as received by the finishing plant from the looms of the mill. It is water-repellent and discolored, due to waxes, pectin, and colored bodies. Some sizing is also present.

Hank. A skein of yarn.

Hard Soap. A sodium soap.

Hard Water. Water containing cations which will precipitate soap.

Herbaceum. A species of Gossypium (cotton) cultivated in India.

Heteropolymer. A polymer composed of units of two or more compounds, one of which will not polymerize by itself.

High Narco. A high-tenacity viscose rayon (North American Rayon Corp.).

Hirsutum. A species of Gossypium (cotton) cultivated in the United States.

Homologous Series. A series of organic compounds belonging to the same family, with a common difference of CH_2 between members.

Hydrocellulose. The result of the first stages of the acid attack, or acid hydrolysis, of cellulose.

Hydrolysis. A chemical reaction in which the ions of water take part, either directly or in the presence of acids or alkalies.

Hydrophobic. Water-repellent.

Hydrophylic. Water-attracting.

Hygram. A high-tenacity viscose rayon (Tubize Corp.).

HYGROSCOPIC. The water-absorbing property of a substance.

HYMOLAL SALT. A salt of a high-molecular-weight alcohol.

IGEPONS. Detergents that are long-chain esters or amides in which a sodium sulfonate group is substituted in the alcohol part of an ester or on the nitrogen of an amide.

IMPACT FACTOR. A number that expresses relative resistance to sudden impacts. It is related to tenacity and elongation in such a way that impact resistance equals ½ the product of tenacity and elongation.

INTERFACIAL TENSION. A force that resists intimate contact between two surfaces.

IODINE NUMBER. The percentage iodine absorbed by an unsaturated substance.

IRON LIQUOR. A solution of ferrous acetate in acetic acid.

KEMPS. Low-quality wool fibers with low felting property, an imperfectly developed medulla, and resistance to ordinary dyes.

KERATIN. The protein of wool.

KETONE. A family of organic compounds having a general formula R—CO—R.

KIER. A piece of equipment in which materials may be boiled under pressure.

KODA. An acetate rayon (Tennessee Eastman Corp.).

LACTOFIL. A Dutch casein fiber.

LANESE. A staple fiber acetate rayon (Celanese Corp.).

LANITAL. An Italian casein fiber.

LANOLIN. Highly purified wool grease.

LIME BOIL. A method used to prepare cotton for bleaching.

LIME MAGMA METHOD. A method for recovering wool grease from waste scouring baths.

LIME SOAP. Calcium soap.

LINEAR POLYMER. A polymer composed of repeated units in long chains, as distinguished from rings.

LINTERS. Very short cotton fibers left on the cotton seed after ginning.

MARKET BLEACH. A term applied to the preparation of white cotton yarn or goods that are to be sold as such, or to be dyed some light color or to be used for cotton prints.

MATESE. A very fine cuprammonium rayon (American Bemberg Corp.).

MEDULLA. The central canal of the wool fiber.

Methylene Blue Number. The number of milliequivalents of methylene blue absorbed by 100 gm of cellulosic material.

Micelle. A bundle of long polymeric molecules held together by secondary valence forces.

Milk of Lime. A suspension of $Ca(OH)_2$ in water.

Milling. A mill operation by which woolen cloths are felted.

Mineral Acids. Inorganic acids.

Modified Cellulose. Cellulose which has been physically changed without excessive chain shortening.

Molar Solution. A solution containing one molecular weight of a chemical compound in one liter of solution.

Mole. Abbreviation for gram-molecular weight.

Molecular Formula. The formula for a chemical compound which shows the atoms present, their proportion, and the molecular weight of the compound.

Monofilament. A man-made filament which is extruded and coagulated as a single filament, as distinguished from yarns or threads composed of several individual filaments extruded from one spinneret.

Monomer. A chemical compound that may be polymerized.

Mungo. A type of British reclaimed wool made from tightly twisted yarns or felted goods.

Narco. A viscose rayon (North American Rayon Corp.).

Neutralization. The reaction between an acid and a base in which equivalent amounts of each take part.

Neutral Soap. A soap that contains an excess of neither alkali, fat, nor fatty acid.

Newbray. A viscose rayon (New Bedford Rayon Corp.).

Newdull. A viscose rayon (New Bedford Rayon Corp.).

Newlow. A viscose rayon (New Bedford Rayon Corp.).

Nitration. A reaction in which nitric acid acts to substitute an NO_2 group in an organic molecule. In cellulose chemistry it is also applied to the formation of cellulose nitrate.

Noils. Short wool fibers left from the combing of wool in the spinning of worsted yarns.

Nonvolatile. A term applied to a liquid that cannot be distilled under ordinary conditions.

Normal Solution. A solution of a chemical compound that contains one equivalent weight of the compound in one liter of solution.

Number of Yarns. Same as Count.

Oleine. Crude oleic acid.

Organzine. A type of thrown silk used for warp and made by twisting grege threads in two stages.

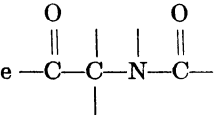
ORIENTATION. A term applied to the arrangement of objects or molecules. In synthetic fiber manufacture it is applied to the operation by which the arrangement of molecules is changed from a random one to a more orderly (parallelized) one.

OSMOSIS. The passage of water through membranes from a lower to a higher concentration. A process by which solutions on opposite sides of a membrane tend to attain equal concentrations.

OXIDATION. A chemical reaction in which atoms show an algebraic increase in valence number.

OXYCELLULOSE. The product obtained during the initial stages of the action of oxidizing agents on cellulosic materials.

PAULY SILK. Cuprammonium rayon.

PEPTIDE LINKAGE. The  $-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{|}{\overset{|}{C}}-\overset{|}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-$ fragment found in protein chains.

PERGLO. A viscose rayon.

PERMANENT HARDNESS. That type of hardness in water which cannot be removed by heat.

PERMUTIT. A synthetic zeolite used in the base exchange method for softening water.

*p*H. The logarithm of the reciprocal of the hydrogen-ion concentration of an aqueous solution. The *p*H of neutral solutions is 7; acid solutions are lower than 7, and alkaline solutions are higher than 7.

PHENOL. An aromatic organic compound having an OH group attached to a benzene ring.

PIMA COTTON. One of the longest staple American cottons, developed in the Salt Creek Valley in Arizona.

PINK SALT. Stannic chloride.

PLASTIC. A material that is susceptible to deformation and is capable of retaining the new form.

PLASTICIZATION. The art of making a material plastic by means of such agencies as heat, pressure, water, solvents, and nonsolvents.

PLASTICIZER. A substance that may be incorporated with a resin to increase the ease of plasticization and that remains in the finished solid material.

PLASTIC STATE. The state in which materials can be converted into a permanent new form by molding, extrusion, laminating, casting, etc.

POLYHYDRIC ALCOHOL. An alcohol with two or more OH groups.

POLYMERIZATION. A reaction that consists of intermolecular combinations that are functionally capable of proceeding indefinitely.

POLYVINYLS. A group of substances formed by the polymerization of various vinyl compounds.

Potassium Quadroxalate. *See* Salts of Lemon.

Ppm. Parts per million or milligrams per liter.

Premier. A viscose rayon (Industrial Rayon Corp.).

Primary Acetate. A highly acetylated cellulose that is insoluble in acetone.

Primary Alcohol. An alcohol having a —CH_2OH group.

Protein. The high polymeric condensation product of amino acids, constituting the most important component of all animal matter.

Psi. Pounds per square inch. The figure used for expressing the tensile strength of materials.

Pure Dye Silk. A term applied to silk that has been weighted 10% or less. It has nothing to do with the color of the silk or any dyes which may have been used.

Pyranose Ring. The ring structure assigned to glucose, containing 5 carbons and 1 oxygen, with a primary alcohol group on carbon 6. (See page 125.)

Pyrolignite of Iron. Ferrous acetate.

Pyrolysis. Decomposition by heat to yield definite chemical compounds.

R. Abbreviation for alkyl group with the general formula C_nH_{2n+1}.

Raflex. A high-tenacity viscose rayon (American Viscose Corp.).

Reclaimed Wool. A general term applied to reprocessed or reused wool.

Red Mordant. Aluminum acetate.

Reducing Sugar. One which has reducing groups or potential reducing groups that will reduce Fehling's solution.

Reduction. A chemical reaction in which atoms suffer an algebraic decrease in valence number.

Reeled Silk. Silk thread made by taking filaments from several cocoons and putting them together in one thread.

Regain. A percentage of the bone-dry weight of a fibrous substance which will be regained when the substance is exposed to an atmosphere of normal humidity.

Regenerated Cellulose. A modified form of cellulose that has been dissolved in some solvent or converted into some cellulose derivative, and subsequently coagulated or precipitated therefrom.

Relative Humidity. A term that describes the amount of moisture in an atmosphere in terms of the percentage of the atmosphere if it were saturated with moisture at the same temperature.

Reprocessed Wool. The resulting fiber when wool has been woven or felted into a wool product which, without ever having been utilized in any way by the ultimate consumer, subsequently has been made into a fibrous state.

REUSED WOOL. The resulting fiber when wool or reprocessed wool has been spun, woven, knitted, or felted into a wool product which, after having been used in any way by the ultimate consumer, subsequently has been converted into a fibrous state.

RIPENING. Any period of time during which systems undergoing slow chemical change are allowed to reach some especially desired condition.

SAKEL. One of the best Egyptian cottons.

SALT BOND. *See* ELECTROVALENT BOND.

SALTING OUT. The precipitation of soap from a concentrated solution by the addition of common salt.

SALTS OF LEMON. Potassium quadroxalate. A crystalline compound of potassium oxalate and oxalic acid, KHC_2O_4—$H_2C_2O_4$—$2H_2O$, or $K_2C_2O_4$—$3H_2C_2O_4$.

SALTS OF SORREL. Same as SALTS OF LEMON.

SAPONIFICATION. The alkaline hydrolysis of an ester, especially a fat.

SAPONIFICATION NUMBER. The number of milligrams of KOH required to saponify 1 gm of fat.

SAPONIFIED RAYON. A high-tenacity acetate rayon.

SCHAPPE SILK. A waste silk spun on the worsted system. It is obtained from the outer and inner parts of cocoons and from pierced cocoons that cannot be reeled.

SCHIFF'S REAGENT. A solution of magenta that has been decolorized by the addition of bisulfites. It is used as a test for aldehydes.

SCHWEITZER'S REAGENT. An ammoniacal solution of copper hydroxide, $Cu(NH_3)_4(OH)_2$.

SCROOP. The characteristic crunching feel and rustling sound associated with silk after it has been finished in a special way.

SEA ISLAND COTTON. A variety of cotton grown on the islands of the sea. It is one of the longest and finest cottons.

SECONDARY ACETATE. A cellulose acetate made by the partial hydrolysis of the primary acetate. It is soluble in acetone.

SECONDARY ALCOHOL. An alcohol having the —CHOH— group.

SECRETION FIBERS. Fibers spun by animals from liquids secreted in glands.

SERICIN. Silk gum; the water-soluble protein spun, along with fibroin, by the silkworm.

SILK GUM. *See* SERICIN.

SILK WASTES. *See* SCHAPPE and BOURETTE SILK.

SNOWKREPE. A cuprammonium rayon (American Bemberg Corp.).

SOAP. The sodium or potassium salt of a mixture of high-molecular-weight fatty acids.

SOAP ACIDS. A mixture of high-molecular-weight organic acids that can be liberated from soap by treatment with a strong mineral acid.

These acids may be saturated or may have one or more double bonds in the chains of carbon atoms.

Soda Ash. Commercial sodium carbonate.

Softs. A term applied to used wool materials that have been woven or knitted from loosely spun yarns.

Soft Soap. A potash soap.

Solute. A substance dissolved in some liquid medium.

Solvent. The liquid medium in which a substance is dissolved.

Soupled Silk. Silk that has had about half its gum removed.

Specific Gravity. The relative weight of a substance compared with an equal volume of water measured at 4° C. For practical purposes, it is the weight in grams of 1 ml of the substance.

Spinneret. A small disk made of platinum or platinum alloys, drilled with tiny funnel-shaped openings. It is used in the extrusion of rayon and synthetic filaments.

Spinning. (1) The operation by which numerous short fibers are assembled and converted into a yarn. (2) The operation of extrusion in which fine streams of solution are forced through a spinneret into a coagulating bath to form very long filaments.

Spun-lo. A viscose rayon (Industrial Rayon Corp.).

Staple. A term associated with the dimensions of length and fineness of a fiber.

Staple Fiber. A term applied to rayon and synthetic fibers that are cut or manufactured in short lengths, comparable to wool and cotton. These staple fibers may be blended with natural fibers and spun into mixed yarns or may be spun alone.

Star Breeze. A cuprammonium rayon (American Bemberg Corp.).

Stearine. Crude stearic acid obtained from wool grease.

Stiffness Factor. In a fiber, the quotient of tenacity divided by elongation.

Stoichiometry. A branch of chemistry dealing with the molecular proportions in which compounds react.

Stretch-spinning. A special method of spinning rayon in which it is stretched as it is spun.

Structural Unit. That fragment of a high-polymeric substance which is repeated time after time in the chain structure.

Suint. The dried perspiration found on raw wool.

Super Narco. A high-tenacity viscose rayon (North American Rayon Corp.).

Superpolyamide. An extra high-molecular-weight polymer formed by the condensation of diamines with dibasic acids.

Surface Tension. A force inherent in the surface of a liquid which resists an increase in the surface area of the liquid.

Tannin Wool. Wool that has been treated with tannic acid and then fixed with tartar emetic.

Tartar Emetic. Potassium antimonyl tartrate, $K(SbO)C_4H_4O_6$.

Temporary Hardness. Bicarbonate hardness; that form of hardness in water which can be partially removed by heat.

Tempra. A high-tenacity viscose rayon (American Enka Corp.).

Tenacity. A term applied to the strength of single fibers or filaments. It is usually expressed in terms of grams per denier, i.e., the grams tension required to break a fiber of 1 denier size. It is related to stiffness, elongation, and impact resistance in that stiffness factor equals tenacity divided by elongation, and impact resistance equals ½ the product of tenacity and elongation.

Tensile Strength. The weight required to break yarn or cloth. For yarns it is expressed in terms of pounds per square inch and for cloth in terms of pounds required to break a 1-in. strip.

Tertiary Alcohol. An alcohol with the $-\overset{|}{\underset{|}{C}}OH$ group.

Thermoplastic Resins. Those resins which are softened by heat.

Thermosetting Resins. Those which harden when sufficient heat is applied and thereafter are infusible.

Thiozell. A German casein fiber.

Thrown Silk. Silk thread made by twisting several reeled threads together.

Throwster. An operator who produces various threads required for textile use, by doubling and twisting reeled silk.

Tin Crystals. Stannous chloride.

Tin Salt. Stannous chloride.

Tiolan. A German casein fiber.

Titer. A term applied to the mixed fatty acids obtained from a fat or a soap. It is the temperature at which the mixture of acids solidifies.

Titration. A quantitative operation in which an acid is exactly neutralized by a base, or vice versa.

Topochemical Reaction. A reaction that proceeds slowly from layer to layer, inward from the surface of a fibrous or stratified solid.

Tops. The long wool fibers obtained by combing wool for the production of worsted yarns.

Tram. A type of thrown silk used for filling, made by doubling grege threads with a small amount of twist.

Trimer. A polymer formed by the polymerization of three molecules of a monomer.

True Elasticity. The maximum percentage a filament can be stretched (under standard conditions) and still have a 100% elastic recovery.

Tufton. A staple fiber rayon.

Turgidity. A state in which a substance is distended or swollen. In textiles it is usually associated with shrinkage.

Twaddell. A system used for expressing the specific gravity of solutions. Each degree Twaddell is equal to 0.005 specific gravity.

Typp Number. The count or number of a textile yarn expressed as "thousand yards per pound."

Tyron. A high-tenacity viscose rayon (Industrial Rayon Corp.).

Upland Cotton. In general, a cotton grown inland and on high ground.

Vegetable Parchment. An imitation parchment made by the controlled acid peptization and regeneration of paper.

Verdigris. Copper acetate.

Veri-Dul. A viscose rayon (Skenandoa Rayon Corp.).

Vicara. A zein fiber (Virginia Carolina Chemical Corp.).

Vinylidene Resins. Those made by the copolymerization of vinylidene chloride with various vinyl compounds.

Virgin Wool. Wool which has never been used, reclaimed, reworked, reprocessed, or reused from any spun, woven, knitted, felted, manufactured, or used product.

Viscose. (1) A type of rayon. (2) The thick viscous solution of sodium cellulose dithiocarbonate in dilute NaOH used in viscose yarn manufacture.

Viscosity. A property of liquids or solutions associated with their rate of flow, a high viscosity meaning a slow rate and a low viscosity a high rate. It is the converse of fluidity.

Vitala. A high-tenacity viscose rayon (American Enka Corp.).

Volatile. Capable of being distilled.

Weighted Silk. Silk that has had its weight increased by treatment with various reagents.

Woolen. Wool yarns carded and spun from short to medium staple wool. The fibers have a more random and scribbled arrangement than in worsted yarn.

Wool Grease. The natural grease, exuded from oil glands of sheep onto wool fibers.

Wool Shoddy. Reclaimed wool.

Wool Sorting. The operation of separating the wool of one fleece into different qualities.

WORSTED. Wool yarns made from long staple wool, by combing loose wool before spinning, thus parallelizing the fibers to a large extent.

XANTHATION. The reaction by which alkali cellulose is converted into sodium cellulose xanthate by means of carbon disulfide.

YORKSHIRE GREASE. The greasy mixture obtained during the recovery of wool grease from waste scouring liquors by the lime or acid magma method.

ZEOLITE. A siliceous or carbonaceous mineral used in the base exchange method for softening water.

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